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ELECTRON ENERGIES AND EFFECTIVE PAIRWISE INTERACTIONS IN A BINARY ALLOY OF SIMPLE METALS

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By

Timothy Mitchell Hayes

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PREFACE

The author wishes to acknowledge a considerable debt to Dean Harvey Brooks. He not only initially suggested the research problem discussed in this report, but guided the author's efforts throughout this investigation of the properties of alloys. In particular, his knowledge of physical effects in real metals was an invaluable aid to the author.

The author also acknowledges the help and encouragement of Professor Arthur Bienenstock. His continued interest in the problem and willingness to discuss difficulties in the formalism were extremely significant at several stages in the research.

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ABSTRACT

The pseudopotential formalism which has been developed to calculate the properties of periodic crystals is extended to treat the case of a binary alloy with an arbitrary degree of order. A self-consistent screening potential which includes the effect of the total conduction electron charge is derived to first order in a perturbation theory expansion in the pseudopotential. The conduction electron contribution to the total energy of the crystal is expressed to second order in the pseudopotential. The applicability of these perturbation theory expansions is discussed extensively. Expressions for that part of the conduction electron energy which contributes to the ordering energy and for the effective pairwise interactions between the ions in the alloy are derived from the expression for the total energy.

If the conduction electron energy may be expressed accurately to second order in the pseudopotential, we demonstrate that this energy depends only upon correlations between pairs of ions. Otherwise, accurate individual electron energies near band gaps are shown to depend upon correlations between three or more ions for an alloy below its critical temperature.

The procedure for selecting an optimal form for the pseudopotential is examined in detail. A Hermitian pseudopotential is chosen and its advantages are discussed. Our calculations on a 50-50 alloy of lithium and magnesium indicate that the selection of an appropriate pseudopotential is quite important.

Further, the calculations reveal that this formalism may be expected to yield accurate estimates only for those quantities which depend upon the difference between two evaluations at the same ionic volume of a given conduction electron property in the alloy, such as the ordering energy. Therefore, we might calculate with accuracy the differences in cohesive energy between two structures with the same volume per ion, or the alloy resistivity, but not the cohesive energy itself. In addition, the effective pairwise interactions are shown to represent well those interactions in the alloy which contribute significantly to the formation of the superlattice.

CHAPTER ONE

INTRODUCTION

A number of methods have been developed in recent years for the calculation of properties of periodic metallic crystals from fundamental considerations, usually in some version of the Hartree-Fock approximation. The augmented plane wave method, the Green's function method, and the pseudopotential method have been used with remarkable success to treat these periodic crystals. The research described in this thesis has been directed toward the extension of this work to calculate the properties of a metallic binary alloy with an arbitrary degree of order. We might expect that significant changes in the crystalline potential during the formation of a superlattice would occur in the region between the ions where the ionic core potentials overlap considerably. Accordingly, we have not used either the augmented plane wave method or the Green's function method in this work. Both of these procedures traditionally require the replacement of the actual crystalline potential due to the ions with an array of spherically symmetric non-overlapping potentials located at each ion site. This approximation is worst in that very region between the ionic cores which may contribute substantially to the formation of the superlattice. On the other hand, the pseudopotential method allows us to replace the actual potential due to the ions with an array of spherically symmetric potentials which may overlap. This approximation should be fairly good in the region between the cores. Our use of the pseudopotential method

has restricted us to the calculation of the properties of alloys formed of simple metals. Simple metals are those in which the core electrons are much more tightly bound than the valence electrons and in which the charge densities associated with adjacent ionic cores may be realistically assumed not to overlap.

In particular, our development of a formalism based on the pseudopotential method has been directed toward obtaining an expression for the ordering energy of a metallic binary alloy. In this context, the ordering energy of the alloy will mean the difference in internal energy between the completely ordered state and the completely disordered state. We have calculated the electronic contribution to this quantity when the ions are rearranged on the lattice at constant volume and at the absolute zero of temperature. We have also calculated the effective pairwise interactions between the ions in the alloy according to the procedure of W. Harrison [1]. These interactions are a central force approximation for the actual interactions between the ions in the alloy. Therefore, the effective pairwise interactions cannot account for contributions to the total energy of the crystal which depend upon the arrangement of the ions only through the volume per ion. If this central force approximation is reasonable, we have a simple physical representation of a complex interaction. The effective pairwise interactions may accordingly be a very convenient property from which to discuss the formation of the superlattice in an alloy. We shall discuss the validity of representing the actual interaction by such a central force interaction.

The effective pairwise interactions may be considered as a polar interaction between the charges contained in the cells around each ion in the alloy plus a term which accounts for the detailed distribution of the electronic charge in those cells. This first contribution to the effective pairwise interactions forms the basis for the polar model which was developed by N.F. Mott [2]. This model of a binary alloy added greatly to our understanding of the ordering energy of such alloys. Mott assumed that the fundamental source of the ordering energy in beta brass is a polar interaction between the charges contained in each atomic cell. In his model, this contribution to the ordering energy of the crystal is given by a Madelung sum of the interactions between certain effective charges considered as point charges at the ion sites. The effective charge associated with a particular cell consisted of the ionic charge, the electronic charge included in the cell due to an average density of conduction electrons, and the electronic charge included in the cell due to screening. Mott calculated this last contribution to the effective charge using a linearized form of the Thomas-Fermi screening formalism. He estimated the value of the screening constant from the increase in the resistivity of pure copper when small amounts of zinc are added. This procedure yielded an effective charge in each cell of $\pm$ 0.075 electronic charges. The Madelung expression for the energy of such a body-centered cubic system of point charges yields a polar contribution to the ordering energy of -0.0020 rydbergs per ion. Fitting

an exponential exchange interaction between the copper ions to the observed elastic constants of copper, Mott estimated that the exchange interaction contributed -0.0009 rydbergs per ion to the ordering energy. He was able to estimate the ordering energy from the theory of Bragg and Williams [3] using the observed critical temperature. This estimate agreed rather well with Mott's calculated value of -0.0023 rydbergs per ion. While this agreement is noteworthy considering the simplicity of the model, we should note that this energy calculation is extremely sensitive to several adjustable parameters, such as the screening constant. This sensitivity lessens appreciably the significance of the final result.

R. J. Harrison and A. Paskin [4] extended the polar model of Mott by using the more realistic screening model of W. Kohn and S. H. Vosko [5]. In this model, the screening charge density has been shown to equal that predicted by the linearized Thomas-Fermi model plus a term which varies as $\cos(2k_F r)/r^3$. This more sophisticated model leads us to expect a cellular charge of $\pm$ 0.12 electronic charges. If we assume that these charges are located at the ionic sites and may be treated as point charges, we can perform the Madelung sum to obtain a contribution to the ordering energy of -0.0051 rydbergs per ion. This would be somewhat large for the ordering energy, even if we allowed for a reasonable uncertainty in the screening constant which was used. However, we have not considered the contribution to the ordering energy of either the interaction between overlapping

core charge densities on adjacent ions or the volume change during ordering. Accordingly, we are unable to judge the accuracy of this result. Harrison and Paskin noted that the Madelung procedure ignored the information which we have regarding the distribution of the electrons within the atomic cells. Therefore, they added the potential due to the ions, considered as point charges, to the potential due to the screening charge to obtain an effective pairwise interaction between the ions. This interaction was that of central forces since they neglected the van der Waals forces between the ions and since the screening density which they associated with each ion was spherically symmetric. Harrison and Paskin summed this interaction over several sets of neighbors and obtained a contribution to the ordering energy of $-0.0029 \sin(\varphi - 0.28)$ rydbergs per ion. The arbitrary phase factor, φ, was introduced to account for the inaccuracy in finding the proper phase in the expression for the charge distribution using this screening model. While this result is certainly consistent with the result of Mott, it is clearly also consistent with any other result less than or equal to -0.0029 rydbergs per ion. Further, we note that the energy due to the interaction between overlapping core charge densities on adjacent ions may account for one-third of the cohesive energy in noble metals [6]. Therefore, we might expect that this core overlap interaction would be significant in beta brass. Our inability to assess the contribution of this core overlap interaction to the ordering energy in a system such as beta brass prevents a realistic discussion of the

accuracy of a calculation of the conduction electron contribution to the ordering energy.

However, the conduction electron contribution and the point ion contribution should dominate the ordering energy of a binary alloy of simple metals. We might hope that a first-principles calculation of the electronic contribution to the effective pairwise interactions and to the ordering energy of such a system can be meaningfully compared with the results of Harrison and Paskin and with experimental evidence of the ordering energy. All of the well-documented transitions from a completely disordered state to a completely ordered state occur in systems in which the overlap of the core charge densities associated with adjacent ions may contribute significantly to the energy of the system. However, the system of 50-50 lithium-magnesium exhibits a reasonable degree of short range order at room temperatures [7]. Thus lithium-magnesium is an alloy of simple metals which shows a tendency to form a superlattice. Accordingly, we have chosen this system for our numerical calculations.

In Chapter Two, we have extended the work of W. Harrison [8] on the pseudopotential in metals to a complete formalism for calculating the matrix elements of the pseudopotential in a binary alloy with an arbitrary degree of order. We have used the form of the pseudopotential to deduce effective pairwise interactions according to the prescription of Harrison [1]. In Chapter Three, we have discussed the form in which the distribution of the ions on the ionic sites in

the crystal enters into expressions for the electronic band energies, the total electronic energy, and the electronic contribution to the ordering energy. We shall see in this connection that a consistent use of a perturbation expansion of the energy to second order in the pseudopotential yields expressions for these quantities which depend upon the distribution of ions in the crystal only through two-particle correlations. In Chapter Four, we have discussed the validity and effectiveness of various forms of the pseudopotential and chosen a suitable form for a calculation. We have discussed in Chapter Five the procedure we have followed in performing an actual calculation using our formalism. Finally, we have calculated the electronic contributions to the effective pairwise interactions and the ordering energy of a 50-50 alloy of lithium and magnesium. The validity of the concept of effective pairwise interactions has been discussed. The effective pairwise interactions which we have obtained do not have the simple form predicted by Harrison and Paskin. The ordering energy is found to be compatible with the experimental data on the system.

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Chapter Two

THE EFFECTIVE PAIRWISE INTERACTIONS AND THE FORMULATION OF THE ALLOY PROBLEM

Our ability to discuss fruitfully the ordering of a metallic alloy in terms of effective pairwise interactions depends upon the accuracy with which we may approximate the significant interactions in the ordering process with central forces between the ions. The elastic properties of metallic crystals fail to satisfy the Cauchy relations, which establish a connection between the compressibility and the shear constants. The Cauchy relations may be shown to be satisfied for any crystal with inversion symmetry if the interactions among the conduction electrons and ions may be expressed exactly in terms of effective central forces between the ions [1]. Accordingly, we may interpret the failure of the elastic properties of a metallic crystal to satisfy the Cauchy relations as a measure of the general insufficiency of central force expressions for the interactions in the crystal. However, this failure in a metallic crystal is largely attributed to the significant contribution of the free electron energy to the cohesive energy. The free electron energy is the total energy of a gas of free electrons, the density of which is equal to the average density of conduction electrons in the metallic crystal. Since this energy is invariant during changes in the structure carried out at constant volume, it will affect the compressibility and other volume-dependent properties, but not the shear constants and other properties dependent upon structure changes at constant volume. Accordingly,

the interactions in metallic crystals may be such that the effective central force interactions might approximate well those properties which depend upon structure changes at constant volume, such as the shear constants or the ordering energy. Yet there may be non-central force interactions, such as that arising from the free electron energy, which prevent an effective central force approximation from accurately predicting volume-dependent properties. These same non-central force interactions would also prevent the Cauchy relations from being satisfied. We may now proceed with our discussion of the effective pairwise interactions in a metallic binary alloy, having reason to believe that such a central force approximation might yield a fruitful discussion of the formation of the superlattice.

The effective pairwise interactions between the ions may be conveniently divided into two contributions. The first contribution arises through the direct Coulomb interaction between the ions, considered as point charges. This treatment specifically neglects the van der Waals interactions between the cores and the interactions due to any overlap of the charge densities associated with adjacent cores. This last approximation is consistent with our use of the pseudopotential method. The second contribution arises through the indirect interaction between the ion cores by means of the conduction electron gas. The contribution to the ordering process due to this interaction may be derived from that part of the total conduction electron energy which varies when the ions in the crystal are rearranged at constant

volume. In his extensive exploration of the nature of pseudopotentials, W. Harrison [2] was able to express the structure-dependent part of the total conduction electron energy in the case of a single-element crystal as

$$\sum_{\{\underline{q}\}}{}' S(\underline{q})\, S^*(\underline{q})\, E(\underline{q}) \tag{2.1}$$

where

$$E(\underline{q}) \equiv \frac{2\Omega_0}{(2\pi)^3} \int_{\substack{\text{Fermi}\\ \text{Volume}}} d^3k \, \frac{\langle \underline{k}|W|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2}$$

$$- \frac{\Omega_0}{16\pi} |\underline{q}|^2 \, |\langle \underline{q}|V^{SC}|0\rangle|^2 \tag{2.2}$$

and

$$S(\underline{q}) \equiv \frac{1}{N} \sum_{\{\underline{R}\}} e^{-i\underline{q}\cdot\underline{R}} \tag{2.3}$$

The sum over the set $\{\underline{R}\}$ which occurs in Equation (2.3) is a sum over all of the ionic sites in the crystal. We should emphasize that expressions (2.1) and (2.2) are the result of a consistent perturbation theory expansion of the total conduction electron energy to second order in the pseudopotential. The inclusion of higher order terms in the pseudopotential would add other structure dependent contributions to the energy. The essential features of Equation (2.1) are that the structure factor, denoted by $S(\underline{q})$, is dependent only upon the positions of the ions and not their nature, while the energy-wavenumber characteristic, denoted by $E(\underline{q})$, is dependent only upon the ionic potentials and the average conduction electron density. By comparison between Equation (2.1) and the form of the energy of the direct interaction between the

ions, Harrison was able to deduce that the contribution of the indirect interaction to the effective pairwise interaction is

$$V_{ind}(\underline{r}) = \frac{\Omega_o}{\pi^2} \int_0^\infty dq\, q^2\, E(q)\, \frac{\sin(qr)}{qr} \tag{2.4}$$

Thus the indirect interaction follows directly from a knowledge of the energy-wavenumber characteristic given by Equation (2.2). We must emphasize that the derivation of a structure-independent expression for $V_{ind}(\underline{r})$ is contingent upon neglecting all terms in the total electron energy of third order or higher in the pseudopotential. If we were to include terms in the energy of order higher than second in the pseudopotential and to express the energy as in Equation (2.1), then $E(q)$ and $V_{ind}(\underline{r})$ would both be structure dependent. This would not yield a central force approximation to the interactions in the crystal during ordering since central forces must depend only upon the distances separating the ions. This close relationship between the use of perturbation theory and the derivation of central force interactions will be of importance later in this chapter.

We shall now proceed in an analogous fashion to derive expressions for the structure dependent part of the electronic energy and for the effective pairwise interactions which are appropriate to the alloy problem. The derivation is similar in many ways to the treatment in reference [2] by W. Harrison for a single-element crystal, but there are important differences which bear examination. We acknowledge here the overriding influence of Harrison's work and will reference only major points hereafter.

Introduction of the Pseudopotential

We wish to determine the conduction electron eigenstates of a crystalline Hamiltonian,

$$H(\underline{r},\underline{r}') = T(\underline{r})\,\delta(\underline{r}-\underline{r}') + V^{I}(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') \; . \tag{2.5}$$

We shall generally refer to non-local operators merely by the appropriate symbol, such as H for the Hamiltonian. The non-locality of the operator in $\underline{r}$-space will be understood. In compliance with conventions regarding Dirac bra and ket notation, we shall denote the eigenstates of H by n, the eigenvalues of H by E_n, and the eigenfunctions of H by $\langle \underline{r}|n\rangle$. The significance of the notation is best summarized by the following equivalences:

$$\langle \underline{r}|H|\underline{r}'\rangle \equiv H(\underline{r},\underline{r}') \; ; \tag{2.6}$$

$$\langle \underline{r}|H|n\rangle \equiv \int d\underline{r}'\; H(\underline{r},\underline{r}')\langle \underline{r}'|n\rangle \; ; \tag{2.7}$$

$$\langle n'|H|n\rangle \equiv \int d\underline{r} \int d\underline{r}'\langle n'|\underline{r}\rangle\, H(\underline{r},\underline{r}')\langle \underline{r}'|n\rangle \; . \tag{2.8}$$

The relationship between H and its eigenstates is such that

$$H|n\rangle = E_n|n\rangle \; . \tag{2.9}$$

Returning to Equation (2.5), we may denote the non-local potential due to all of the ions and electrons in the crystal by V. This potential may be separated according to

$$V = \tilde{V}_L + V^{I} + V^{EL} \; . \tag{2.10}$$

V^{I} is the sum of all of the Hartree-Fock potentials of the ions in the

crystal less the spatial average of the Hartree potentials of the ions. We have neglected the influence of correlation between the electrons of the ion cores and the conduction electrons. Since the motions of the core electrons are much more rapid than those of the conduction electrons, the influence of the core electrons on the conduction electrons may be very well represented in terms of an average potential due to the core electrons, such as a Hartree-Fock potential. Thus V^I should well represent the potential due to the ionic cores as seen by the conduction electrons. V^{EL} is the non-local potential due to the conduction electrons in the crystal less the spatial average of the Hartree potential due to these conduction electrons. We must later make an approximation for the many-particle potential denoted by V^{EL} which will enable us to reduce the many-body problem of solving for the eigenstates of Expression (2.5) to a one-electron problem. The potential denoted by $\bar{V}_L$ is the average over the crystal of the potentials due to the nuclei and the Hartree potentials of the core and conduction electrons. In accordance with these definitions we may write T as

$$T \equiv -\underline{\nabla}_{\underline{r}} \cdot \underline{\nabla}_{\underline{r}} + \bar{V}_L \ , \tag{2.11}$$

in atomic units, which we shall use throughout this work. One set of eigenvalues of the operator T is the complete set of plane waves. If the volume of the crystal is Ω, we may write the eigenfunction associated with the plane wave $\underline{k}$ as

$$\langle \underline{r} | \underline{k} \rangle = e^{i\underline{k}\cdot\underline{r}}/\Omega^{\frac{1}{2}} \ . \tag{2.12}$$

The eigenvalue of T associated with this plane wave is $(|\underset{\sim}{k}|^2 + \bar{V}_L)$ in atomic units.

In order to apply the pseudopotential method, which may be regarded as a generalization of the orthogonalized plane wave method, to the determination of the eigenstates of H, we must assume that each eigenstate of H may be classified into one of the two following categories. The wavefunctions of those states in the first category must be sufficiently localized about their respective nucleii that they may be very closely approximated by the corresponding atomic wavefunction. The eigenvalues of those states in the second category must be sufficiently free-electron like that they may be readily determined using the pseudopotential method. If there exist some eigenstates of H which may not be placed in the first category, and yet whose properties are not amenable to a pseudopotential method treatment, we may not use the pseudopotential method for this problem. As a specific example, we might consider those crystalline states which arise from the 3d shell states of a copper atom when metallic copper is formed. These states have eigenfunctions which are not sufficiently well localized about the nucleii to be approximated well by the 3d shell wavefunctions. These eigenstates interact too strongly with other states in the crystal. On the other hand, the sums which must be evaluated to determine either the eigenfunctions or the eigenvalues of such states using the pseudopotential method converge very slowly. Accordingly, we should not use the pseudopotential method to treat such a problem. The

necessity of classifying the eigenstates into these categories is the most serious restriction on the use of the pseudopotential method.

Once we have made the classification of the eigenstates, we shall refer to those states of H which fall into the first category as core states, denoted by c, and assume that the eigenfunctions of these states are identical with the corresponding atomic wavefunctions. Those states which fall into the second category will be referred to as valence states, denoted by v. In their discussion of the general theory of pseudopotentials, Austin, Heine, and Sham [3] established the properties of a general pseudo-Hamiltonian of the form

$$H_p(\underline{r},\underline{r}') \equiv T(\underline{r})\ \delta(\underline{r}-\underline{r}') + W(\underline{r},\underline{r}') \ , \tag{2.13}$$

where

$$W(\underline{r},\underline{r}') = V^{I}(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') + \Sigma_c \langle \underline{r}|c\rangle f_c(\underline{r}') \ , \tag{2.14}$$

and $f_c(\underline{r}')$ is a completely arbitrary function of $\underline{r}'$ and the parameter "c". The sum over c in Equation (2.14) extends over all of the core states of H as given in Equation (2.5). The essential properties of H_p result from the absence of valence states from the sum in Equation (2.14) and may be summarized as follows: the "core" eigenstates of H_p, denoted by $\bar{c}$, are linear combinations of the core eigenstates of H; the "valence" eigenvalues of H_p are identical with the valence eigenvalues of H; the "valence" eigenfunctions of H_p, denoted by $\bar{v}$, are related to the valence eigenfunctions of H by

$$|v\rangle = |\bar{v}\rangle - \Sigma_c\ |c\rangle\langle c|\bar{v}\rangle \ . \tag{2.15}$$

When applied to the eigenstates of H_p, the terms "core" and "valence" mean no more than is implied in the relationships above. The particular functional dependence which we choose for $f_c(\underline{r}')$ in a given calculation is determined by the requirements of that calculation. In general, $f_c(\underline{r}')$ will be chosen to optimize in some sense the convergence of a procedure for determining the eigenstates. We will now proceed with our derivation using the general form of the pseudopotential, W, given by Expression (2.14).

Separation of the Unscreened Pseudopotential

The unscreened pseudopotential is that part of the crystalline pseudopotential which does not arise directly from the conduction electron gas. Accordingly, if we denote the unscreened pseudopotential by W^o, we may define it formally by $W = W^o + V^{EL}$. The unscreened pseudopotential depends on V^I, which consists of the Hartree-Fock potentials of all of the ion cores less the average of the Hartree potential of the cores. In accordance with our discussion of the core states of H, we shall consider the ion cores as consisting of the nucleii and those electrons which are denoted as core electrons. The Hartree-Fock potential associated with a single ion of type i located at the origin may be written as

$$v_i(\underline{r},\underline{r}') = \frac{2Z}{|\underline{r}|}\,\delta(\underline{r}-\underline{r}') - 2\Sigma_c \int d\underline{r}''\,\frac{\langle c|\underline{r}''\rangle\langle \underline{r}''|c\rangle}{|\underline{r}-\underline{r}''|}\,\delta(\underline{r}-\underline{r}') + 2\Sigma_c\,\frac{\langle \underline{r}|c\rangle\langle c|\underline{r}'\rangle}{|\underline{r}-\underline{r}'|}\,, \tag{2.16}$$

where the sum over c extends only over the core states associated with this particular ion. We recall that we have assumed that the core eigenfunctions may be very closely approximated by the corresponding atomic wavefunctions. In general, of course, we would expect that the core eigenfunctions on an ion would depend upon the local configuration of ions. If the potential seen by the core state on the isolated neutral atom is denoted by V_a, then the additional potential which the core state sees in the crystal is $(V - V_a)$. This additional potential should be quite slowly varying in the vicinity of the core. If the core wavefunctions are very localized about the nucleus, then this additional potential may be considered essentially constant over the region of the core. This approximation is often called the small core approximation. Under these conditions, the core wavefunction will not be changed in the crystal but the core eigenvalue will be shifted by an amount equal to $(V - V_a)$ evaluated at the nucleus. Accordingly, we may use atomic eigenfunctions at all times for the core states. Then the ionic Hartree-Fock potential for an A ion, for instance, in an AB alloy will be the same for every A ion in the system, since it depends only upon the nuclear charge and the core eigenfunctions through Equation (2.16). We must introduce some appropriate notation to describe the effect of this property upon V^I. The set $\{\underline{R}\}$ will describe the entire set of ionic sites in the crystal from some convenient site chosen as origin. The function $\sigma(\underline{R})$ is defined as follows:

$$\sigma(\underline{R}) = +1 \quad \text{if the site } \underline{R} \text{ contains an A ion;}$$

$$\sigma(\underline{R}) = -1 \quad \text{if the site } \underline{R} \text{ contains a B ion.} \tag{2.17}$$

All of the information regarding the configuration of ions on the sites $\{\underline{R}\}$ is contained in $\sigma(\underline{R})$. The invariance of the ionic potentials allows us to use these definitions to write

$$V^I(\underline{r},\underline{r}') + \bar{V}_L^I = \frac{1}{2}\Sigma_{\{\underline{R}\}}[(1+\sigma(\underline{R}))v_A(\underline{r}-\underline{R},\underline{r}'-\underline{R}) + (1-\sigma(\underline{R}))v_B(\underline{r}-\underline{R},\underline{r}'-\underline{R})] , \tag{2.18}$$

where $\bar{V}_L^I$ is the spatial average of the sum of the potentials of all the nucleii and the Hartree potentials of the core electrons.

Having found a suitable expression for V^I, we may turn our attention to the other component of W^o, the sum over core states in Expression (2.14). This sum over the core states consists of a sum over the set $\{\underline{R}\}$ as well as the sum over all of the core states associated with the ion at each point $\underline{R}$. Displaying these sums explicitly, we may write the sum as

$$\Sigma_{\{\underline{R}\}} \Sigma_{nlms} \langle \underline{r}-\underline{R}|nlms;\underline{R}\rangle \, f_{nlms;\underline{R}}(\underline{r}'-\underline{R}) . \tag{2.19}$$

The invariance which we assumed in the ionic potentials is typical of the invariance which must be assumed in other terms of the pseudopotential in order to separate W in analogy with the treatment of the single-element crystal by Harrison. The separation of each matrix element of the pseudopotential into a structure-dependent factor and a structure-independent factor is central to the results of pseudo-

potential theory, in particular to the derivation of an effective pairwise interaction. To enable the separation of W, we wish to place Expression (2.19) into a form similar to that of the right-hand side of Expression (2.18). The core eigenfunctions have already been assumed to depend only upon the type of ion with which they are associated. We will wish to choose a functional form for $f_c(\underline{r})$ which will optimize the pseudopotential in some sense. Accordingly, we will impose the least restricting condition upon $f_c(\underline{r})$ and require only that, for a given arrangement of ions in the crystal, $f_c(\underline{r})$ be independent of the position which that type of ion might occupy. In general, the $f_c(\underline{r})$ which truly optimizes the pseudopotential might depend in detail upon the position of the ion core in the lattice. We have therefore restricted the freedom which we have in choosing $f_c(\underline{r})$. This is not to be confused with the assumption that the core states are invariant, and is not an assumption in any sense. We may later find it convenient to further restrict $f_c(\underline{r})$ so that it is invariant with respect to rearrangement of ions at constant volume. The lesser restriction upon $f_c(\underline{r})$ is sufficient to allow us to write Expression (2.19) as

$$\frac{1}{2}\Sigma_{\{\underline{R}\}}[(1+\sigma(\underline{R}))\,\Sigma_{nlms}\langle\underline{r}-\underline{R}|nlms;A\rangle\, f_{nlms;A}(\underline{r}'-\underline{R}) + (1-\sigma(\underline{R}))\,\Sigma_{nlms}\langle\underline{r}-P|nlms;B\rangle\, f_{nlms;B}(\underline{r}'-\underline{R})]\,. \qquad (2.20)$$

Equations (2.18) and (2.20) allow us to write W^o as

$$w^{o}(\underline{r},\underline{r}') = \frac{1}{2}\Sigma_{\{\underline{R}\}}\Big[(1+\sigma(\underline{R}))w_A^{o}(\underline{r}-\underline{R},\underline{r}'-\underline{R}) + (1-\sigma(\underline{R}))w_B^{o}(\underline{r}-\underline{R},\underline{r}'-\underline{R})\Big] - \bar{V}_L^{I} , \tag{2.21}$$

where

$$w_i^{o}(\underline{r},\underline{r}') \equiv v_i(\underline{r},\underline{r}') + \Sigma_{nlms;s}\langle \underline{r}|nlms;i\rangle\, f_{nlms;i}(\underline{r}') . \tag{2.22}$$

Equation (2.22) defines an unscreened ionic pseudopotential associated with an ion of type i.

Since we will eventually attempt to express the valence eigenfunction of H_p in terms of plane waves, we will need the matrix elements of the total pseudopotential between plane waves. As may be seen from Equation (2.21), the unscreened part of these matrix elements will involve integrals of the type

$$\frac{1}{\Omega}\int_{\Omega} d\underline{r} \int_{\Omega} d\underline{r}'\; e^{-i(\underline{k}+\underline{q})\cdot\underline{r}}\; w_i^{o}(\underline{r}-\underline{R},\underline{r}'-\underline{R})e^{i\underline{k}\cdot\underline{r}} . \tag{2.23}$$

Such integrals are common in band theory. Translating the origins in the spaces $\underline{r}$ and $\underline{r}'$ to the point $\underline{R}$, we introduce a factor $\exp(-i\underline{q}\cdot\underline{R})$ before the integral. Since the volume of the crystal may be allowed to become arbitrarily large at our convenience, we may neglect any boundary effects which arise from the translations. In practice, the integrals of the ionic potentials will be performed over all space. If the crystal volume, Ω, contains N ions, the ionic volume, denoted by Ω_o, is equal to Ω/N. Expression (2.23) may be written now as

$$\frac{1}{N} e^{-i\underline{q}\cdot\underline{R}}\, \langle \underline{k}+\underline{q}|w_i^{o}|\underline{k}\rangle_{\Omega_o} , \tag{2.24}$$

where

$$\langle \underline{k}+\underline{q}|w_i^o|\underline{k}\rangle_{\Omega_o} \equiv \frac{1}{\Omega_o}\int_\Omega d\underline{r}\int_\Omega d\underline{r}'\; e^{-i(\underline{k}+\underline{q})\cdot\underline{r}}\; w_i^o(\underline{r},\underline{r}')\; e^{+i\underline{k}\cdot\underline{r}'} . \tag{2.25}$$

We are now able to write the matrix elements of W^o as

$$\langle \underline{k}+\underline{q}|W^o|\underline{k}\rangle = \frac{1}{2}\Sigma_{\{\underline{R}\}}\Big[(1+\sigma(\underline{R}))\; e^{-i\underline{q}\cdot\underline{R}}\;\langle \underline{k}+\underline{q}|w_A^o|\underline{k}\rangle_{\Omega_o}$$
$$+ (1-\sigma(\underline{R}))e^{-i\underline{q}\cdot\underline{R}}\;\langle \underline{k}+\underline{q}|w_B^o|\underline{k}\rangle_{\Omega_o}\Big] - \bar{V}_L^I\,\delta_{\underline{q},o} \; . \tag{2.26}$$

The outstanding feature of Expression (2.26) is that the $\underline{R}$ dependence of the terms in the brackets is explicitly displayed in terms of the exponential and $\sigma(\underline{R})$, in analogy with the case of a single-element crystal. For the alloy problem, it is logical to consider some suitable average and difference potentials. Harrison [1] has reached the same conclusion independently. Accordingly, if the total number of A ions in the alloy is xN, we may define an average unscreened pseudopotential,

$$\langle \underline{k}+\underline{q}|\bar{w}^o|\underline{k}\rangle \equiv x\langle \underline{k}+\underline{q}|w_A^o|\underline{k}\rangle_{\Omega_o} + (1-x)\langle \underline{k}+\underline{q}|w_B^o|\underline{k}\rangle_{\Omega_o} \; , \tag{2.27}$$

and a difference unscreened pseudopotential,

$$\langle \underline{k}+\underline{q}|\Delta w^o|\underline{k}\rangle \equiv \frac{1}{2}\langle \underline{k}+\underline{q}|w_A^o|\underline{k}\rangle_{\Omega_o} - \frac{1}{2}\langle \underline{k}+\underline{q}|w_B^o|k\rangle_{\Omega_o} \tag{2.28}$$

Introducing $\langle\sigma\rangle_{\underline{R}}$, the average of $\sigma(\underline{R})$ over the crystal,

$$\langle\sigma\rangle_{\underline{R}} \equiv \Sigma_{\{\underline{R}\}}\frac{\sigma(\underline{R})}{N} = (+1)x + (-1)(1-x) = 2x-1 \; , \tag{2.29}$$

we can rewrite Equation (2.26) as

$$\langle \underline{k}+\underline{q}|W^o|\underline{k}\rangle = \langle \underline{k}+\underline{q}|\bar{w}^o|\underline{k}\rangle\left[\Sigma_{\{\underline{R}\}}\frac{e^{-i\underline{q}\cdot\underline{R}}}{N}\right] - \bar{V}_L^I\,\delta_{\underline{q},o}$$
$$+ \langle \underline{k}+\underline{q}|\Delta w^o|\underline{k}\rangle\left[\Sigma_{\{\underline{R}\}}\frac{(\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})e^{-i\underline{q}\cdot\underline{R}}}{N}\right] . \tag{2.30}$$

In order to discuss the sums over $\{\underline{R}\}$ which occur in Equation (2.30), we must introduce certain concepts of reciprocal space [5]. In general, reciprocal space vectors such as $\underline{q}$ or $\underline{k}$ may be any of those wavevectors which satisfy the periodic boundary conditions of Born and von Karman. The set $\{\underline{K}\}$ is a subset of these reciprocal space wavevectors to which we will refer as the set of reciprocal lattice vectors associated with $\{\underline{R}\}$. We recall that the set $\{\underline{R}\}$ was defined as describing the set of sites in the crystal which contain ions, and is not related to the symmetry of the filled sites. The set $\{\underline{K}\}$ consists of all those vectors $\underline{k}$ such that $\exp(-i\underline{k}\cdot\underline{R}) = 1$ for all members of the set $\{\underline{R}\}$, and corresponds to those vectors associated with Bragg reflections in a single-element crystal. The sum of $\exp(-i\underline{k}\cdot\underline{R})$ over the set $\{\underline{R}\}$ is just N if $\underline{k}$ is a member of $\{\underline{K}\}$. Otherwise, the phases of the exponentials are such that the sum cancels. Therefore the first sum in Equation (2.30) is just the well-known Kronecker delta,

$$\Sigma_{\{\underline{R}\}} \frac{e^{-i\underline{q}\cdot\underline{R}}}{N} = \delta_{\underline{q},\{\underline{K}\}} \; . \tag{2.31}$$

We shall now define $F(\underline{q})$ by

$$F(\underline{q}) \equiv \Sigma_{\{\underline{R}\}} \frac{(\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})\, e^{-i\underline{q}\cdot\underline{R}}}{N} \; . \tag{2.32}$$

We may note immediately that Expression (2.31) is just the structure factor of Harrison's formalism, as defined by Equation (2.3). Since the exponential factor in Equation (2.32) is unity for all members of $\{\underline{R}\}$ if $\underline{q}$ is a member of $\{\underline{K}\}$, we may further observe that $F(\underline{q})$ vanishes

for all $\underline{q}$ which belong to $\{\underline{K}\}$. Accordingly, either Expression (2.31) or Expression (2.32) will vanish for a given value of $\underline{q}$. A given matrix element of the unscreened pseudopotential will depend upon either the average or the difference unscreened pseudopotential, and never both. Further, if we associate the constant potential $\bar{V}_L^I$ with the diagonal matrix element of the average unscreened pseudopotential, we observe that a given matrix element of the unscreened pseudopotential is always the product of a structure-dependent factor, such as $F(\underline{q})$ or the Kronecker delta, with a structure-independent factor, such as a matrix element of $\bar{w}^o$ or Δw^o. In addition, the structure-dependent factor never depends upon the form of the ionic potentials. It is this separability of the matrix elements into these two factors which is so central to the results of pseudopotential theory and this work in particular. This separability, when demonstrated for the screened pseudopotential, will lead directly to a structure-independent energy-wavenumber characteristic and to structure-independent effective pairwise interactions. From Equations (2.31) and (2.32), we may write the matrix elements of the unscreened pseudopotential as

$$\langle \underline{k}+\underline{q}|W^o|\underline{k}\rangle = \delta_{q,\{\underline{K}\}}\langle \underline{k}+\underline{q}|\bar{w}^o|\underline{k}\rangle + F(\underline{q})\langle \underline{k}+\underline{q}|\Delta w^o|\underline{k}\rangle - \bar{V}_L^I\,\delta_{\underline{q},o} \; . \quad (2.33)$$

The virtual crystal approximation has been widely used to treat the case of a disordered binary alloy. In this approximation, the actual potential due to the ions in the crystal is replaced by a periodic array of ionic potentials which are the weighted average of the two

different ionic potentials in the alloy. This approximate potential differs from the potential represented by the first term in Equation (2.33) by only the orthogonalizing terms which have been added to the ionic potentials to obtain the unscreened pseudopotential. Thus the first term in Equation (2.33) represents the potential of a virtual crystal of pseudo-ions. As we would expect, the difference unscreened pseudopotential vanishes in the limit as the two types of ions in the alloy become identical and we obtain the appropriate unscreened pseudopotential for a single-element crystal. Thus the effect of alloying is to split the matrix elements of the unscreened pseudopotential into two parts. The first part is a virtual crystal approximation for the potential of the pseudo-ions, and depends upon only the configuration of the ionic sites in the crystal. The second part is a correction to the virtual crystal approximation which accounts for the difference between the ionic pseudopotentials and depends in detail upon the arrangement of the ions on the ionic sites. We should note at this point that the average and difference unscreened pseudopotentials, as we have defined them, are not strictly independent of the order of the system since we have not restricted $f_c(\underline{r})$ so that it may not vary from configuration to configuration. We may find it convenient at some later time to restrict $f_c(\underline{r})$ to being invariant during rearrangements of the ions at constant volume. Under that restriction, the average and difference unscreened pseudopotentials would be truly constant during variations in the configuration of the ions at constant ionic volume. In any case, we expect that the ordering process will affect

the pseudopotential most strongly through variations in $F(\underline{q})$, not $f_c(\underline{r})$. Let us now turn to the calculation of the matrix elements of the screening potential.

Derivation of the Screening Potential

The remaining contribution to the pseudopotential, W, is the potential due to the conduction electrons. As we indicated earlier, an exact evaluation of this potential would require the solution of a difficult many-body problem. In fact, the energy of a homogeneous electron gas at metallic densities is still a problem of great theoretical interest. Accordingly, we must make an approximation which will enable us to estimate the potential due to the conduction electrons, which we denote by V^{EL}. The greatest contribution to V^{EL} is the Hartree potential of the conduction electrons. This is the Coulomb potential of that charge density which results from a statistical average over the probability distribution of the electrons. The electrons are treated as being statistically independent in this potential, neglecting the many-body effects. The introduction of the Fock exchange potential accounts for the antisymmetry of the conduction electron many-body wavefunction by raising the energy of those states in which electrons of the same spin are close together. This potential tends to exclude half of the local charge density from the immediate region of a given electron. The correlation effect accounts for the Coulomb repulsion of the individual electrons and is a true many-body correction

to the Hartree-Fock potential. These three contributions completely determine V^{EL}.

An analysis of the effects of exchange and correlation by Harrison [6] suggests that these many-body effects may make a significant contribution to cohesive energies and ordering energies in a pseudopotential calculation, even though they may not affect the total electronic energy greatly. Further, we cannot neglect the correlation potential relative to the exchange potential as we could when we were considering the effect of the core electrons on the conduction electrons. The work of P. Nozières and D. Pines [7] has indicated that the contribution of the correlations among electrons to the energy of a free electron gas at metallic densities is roughly one-fourth of the contribution due to exchange. Correlation effects might be relatively more significant in determining the cohesive energy of a real metal, or the ordering energy of an alloy. Formally, the simplest procedure would be to approximate V^{EL} with the Hartree-Fock potential of the conduction electrons and neglect the effect of correlations. The derivation of the self-consistent electron potential would proceed in direct analogy with the treatment of the Hartree potential which follows. However, an actual calculation of the electron potential in the Hartree-Fock approximation would be greatly complicated by the non-locality of that potential. Due to the uncertainty in the relative significance of the exchange and correlation effects, we could not be confident that the additional work would produce significantly better results. Further, the inclusion of the effects of exchange without those of correlation is well known to

yield poor results for a free electron gas. Since the emphasis of this work is on the special properties of alloys relative to single-element crystals, we have decided not to include the non-local Fock exchange potential without a similar expression for the correlation potential.

A more promising approach to the problem of the exchange and correlation potentials has been suggested by the work of W. Kohn and L.J. Sham [8]. They have developed a formalism for expressing the effects of exchange and correlation in terms of the local density of the conduction electron gas, denoted by n. Their expressions may then be expanded in powers of grad (n). Kohn and Sham have given a local expression for the potentials due to exchange and correlation which they claim neglects only the effects of the fourth and higher powers of grad (n). As we shall demonstrate, we must linearize our expression for the electronic potential in order to obtain a self-consistent solution. In a linear formalism, each Fourier component of the charge density is screened separately. Accordingly, we might expect that the local expression given by Kohn and Sham will not give the proper matrix element of the potential for large $\underline{g}$ components of n since their expression results from an approximation of slowly varying electron density. A linearization of the local expression in terms of the pseudopotential confirms this expectation. The matrix elements of the exchange and correlation potentials do not tend to cancel the matrix elements of the Hartree potential as $\underline{g}$ becomes very large, but continue to grow in influence. Unfortunately, this deviation from the expected asymptotic behavior appears to extend well into the region in $\underline{g}$ space

where we would expect the correlation and exchange effects to contribute significantly to the ordering process. Rather than guess at a proper interpolation procedure to predict the effects of exchange and correlation in the crucial region, we have decided to neglect the influence of many-body effects on the ordering of our system. This decision was largely the result of our desire to concentrate upon the peculiar properties of an alloy system. Accordingly, we wish to avoid making a questionable approximation of many-body effects when such an approximation might dominate our results. Although the work of Kohn and Sham may eventually lead to a useful approximation of the effects of exchange and correlation, we will limit our treatment to an approximation of V^{EL} in terms of the Hartree potential.

In our derivation of the Hartree potential, denoted by V^{sc}, we shall introduce several approximations. In each case, we shall emphasize the aim of the approximation and the restrictions which it imposes upon the accuracy and validity of the final result. We may begin by writing Poisson's equation for the screening potential in terms of the conduction electron charge density as

$$\nabla_{\underline{r}} \cdot \nabla_{\underline{r}} V^{sc} = 8\pi n_{CE} = -8\pi \Sigma_{\{v\}} \langle \underline{r}|v\rangle\langle v|\underline{r}\rangle \ . \tag{2.34}$$

The sum over $\{v\}$ in Equation (2.34) is over all of the occupied electronic eigenstates of H. The contribution to the potential due to the average conduction electron charge density has already been included in T as part of $\bar{V}_L$. In order to find the effect of the spatially varying part

of the conduction electron charge density, we shall take the matrix elements of Equation (2.34) between plane waves $\underline{k+q}$ and $\underline{k}$. Since V^{sc} is manifestly local, its matrix elements are a function only of the difference between the wave vectors. Accordingly, we may write the off-diagonal matrix elements of V^{sc} as

$$\langle \underline{q}|V^{sc}|0\rangle = \frac{8\pi}{|\underline{q}|^2}\,\Sigma_{\{v\}}\langle \underline{q}|(\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle)|0\rangle \ . \tag{2.35}$$

Using Equation (2.15), we may express $\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle$ in terms of the pseudo-valence state $\bar{v}$ as

$$\begin{aligned}\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle = \langle \underline{r}|\bar{v}\rangle\langle \bar{v}|\underline{r}\rangle &- \Sigma_c\langle \underline{r}|c\rangle\langle c|\bar{v}\rangle\langle \bar{v}|\underline{r}\rangle \\ &- \Sigma_c\langle \underline{r}|\bar{v}\rangle\langle \bar{v}|c\rangle\langle c|\underline{r}\rangle \\ &+ \Sigma_c\,\Sigma_{c'}\langle \underline{r}|c\rangle\langle c|\bar{v}\rangle\langle \bar{v}|c'\rangle\langle c'|\underline{r}\rangle \ ,\end{aligned} \tag{2.36}$$

where $\bar{v}$ satisfies the pseudo-Hamiltonian equation,

$$H_p|\bar{v}\rangle = T|\bar{v}\rangle + W|\bar{v}\rangle = E_v|\bar{v}\rangle \ . \tag{2.37}$$

We wish to obtain a self-consistent expression for the matrix elements of V^{sc}. The most obvious method for obtaining this expression is an iterative procedure. We begin by assuming a set of matrix elements of V^{sc}, which may be combined with W^o to yield an expression for the screened pseudopotential. Equation (2.37) then allows us to calculate a set of $\bar{v}$, which may be substituted into Equation (2.36) and combined with Equation (2.35) to yield a new set of matrix elements V^{sc}. Hopefully, each iteration of this procedure will bring us closer to the actual self-consistent set of matrix elements of V^{sc}. But let

us examine the size of the secular matrix which must be solved to yield the $\bar{v}$. In a crystal which can be described in terms of a small repeating cell, such as a single-element crystal or an ordered alloy, we may describe the locations of the repeating cells by a set of vectors, $\{\underline{R}_s\}$, which is a subset of $\{\underline{R}\}$. As in the case of $\{\underline{R}\}$, we can construct a set of vectors $\{\underline{K}_s\}$ in reciprocal space such that $\{\underline{K}_s\}$ contains all those vectors such that $\exp(-i\underline{K}_s \cdot \underline{R}_s) = 1$ for all members of $\{\underline{R}_s\}$. The symmetry described by $\{\underline{R}_s\}$ in real space is manifested in reciprocal space by the vanishing of all the matrix elements of the pseudopotential between two plane waves unless their wave vectors differ by a member of $\{\underline{K}_s\}$. This result is well-known for the actual crystalline potential and has been demonstrated [2] for a single-element pseudopotential. The generalization to the case of an ordered alloy follows readily and we shall not dwell upon it here. In practical applications of the iterative procedure we discussed above, we can truncate the set of $\{\underline{K}_s\}$ vectors which we choose to consider in a given secular matrix to a manageable set since the interaction between plane waves $\underline{k}$ and $\underline{k + K_s}$ decreases rapidly for large values of $|\underline{K}_s|$. In the case of an alloy which is not in an ordered state, however, we must consider the matrix elements of the pseudopotential between all members of the set $\{\underline{k}\}$, since none of them vanish through symmetry. The dimension of our secular matrix must then be larger than in the ordered case by roughly a factor of N. N is the number of ions in the alloy and is arbitrarily large. The

secular matrix would be unmanageable for this general case and we could not use the method described above.

One other problem arises when we attempt to arrive at a self-consistent expression for the matrix elements of V^{sc} using a method which requires the direct solution of a secular matrix equation. The energy of the state $\bar{v}$ obtained from the diagonalization associated with such a solution depends in general upon the products of many matrix elements of the pseudopotential. As we shall demonstrate in the next chapter, these products will involve factors like $F(\underline{q}^1)\, F(\underline{q}^2) \ldots F(\underline{q}^M)$ where $\underline{q}^1 + \underline{q}^2 + \cdots + \underline{q}^M$ is a member of $\{\underline{K}\}$. We shall further demonstrate that even a combination of perturbation theory and the solution of a small secular matrix will still leave the energy of $\bar{v}$ dependent upon at least the product $F(\underline{q}')F(-\underline{q}')$ for all values of $\underline{q}'$ in the set $\{\underline{k}\}$. Since this energy enters into the coefficients of the plane waves in the expansion of $\langle \underline{r}|\bar{v}\rangle$, the least dependence upon $F(\underline{q}')$ which the matrix element $\langle \underline{q}|V^{sc}|0\rangle$ will demonstrate will involve $F(\underline{q}')F(-\underline{q}')$ for all $\underline{q}'$. Therefore, we could never place the matrix elements of V^{sc} in the form of Expression (2.33) unless we were willing to let the average and difference pseudopotentials depend indirectly upon $F(\underline{q}')$. This dependence would destroy all the important properties of the separated form. Recall that we may require the average and difference unscreened pseudopotentials to be completely independent of configuration at constant volume within the assumptions which we made in deriving Expression (2.33). In order to preserve this property in the screened pseudopotential, we must limit our expression for V^{sc} to that which may be obtained from perturbation theory. We may

further note that the general expression for V^{sc} obtained from a method which involves a direct solution of a secular matrix equation would involve products of M $F(\underline{q})$'s, where $M \geq 2$. We shall later show that these products involve M-particle correlation functions. This would further complicate the solution of the secular equation, and the procedure for obtaining V^{sc}.

Turning to perturbation theory, we can hope that our pseudo-states will be more amenable to a perturbation treatment than the actual valence eigenstates. If we expand the pseudo-valence state $\bar{v}$ using plane waves as a basis, and then express the coefficients of the plane waves as a perturbation expansion in the pseudopotential, $W = W^{o} + V^{sc}$, we may write one of the many terms which occur on the right-hand side of Equation (2.35) as

$$\langle \underline{k}+\underline{q}+\underline{q}^{1}|W|\underline{k}+\underline{q}^{2}\rangle\langle \underline{k}+\underline{q}^{2}|W|\underline{k}+\underline{q}^{3}\rangle\cdots\langle \underline{k}+\underline{q}^{M}|W|\underline{k}+\underline{q}^{1}\rangle \ . \tag{2.38}$$

We may regard the matrix elements of W as being known. A term of M'th order in the pseudopotential, such as the one above, will have many products of the matrix elements of V^{sc}. The largest such product which will occur is

$$\langle \underline{q}^{1}|V^{sc}|\underline{q}^{2}\rangle\langle \underline{q}^{2}|V^{sc}|\underline{q}^{3}\rangle \cdots \langle \underline{q}^{M}|V^{sc}|\underline{q}^{1}\rangle \ , \tag{2.39}$$

where the vectors $\underline{q}^{1}, \underline{q}^{2},\ldots,\underline{q}^{M}$ will assume all of the values in $\{\underline{k}\}$. Thus all terms occurring on the right-hand side of Equation (2.35) which are higher than first order in the pseudopotential will give rise to products of two or more matrix elements of V^{sc}. These products will transform the set of equations suggested by Equation (2.35)

into a non-linear set of equations of order N to be solved for the matrix elements of $\overline{V}^{sc}$. In order to avoid such an insolvable set of equations we must restrict the right-hand side of Equation (2.35) to consist only of first order terms in a perturbation theory expansion in the pseudopotential. This restriction is also necessary to avoid obtaining a $\langle \underline{q}|V^{sc}|0\rangle$ which depends upon $F(\underline{q}')$ for all values of $\underline{q}'$, since products like Expression (2.38) involve factors of $F(\underline{q}')$ for all values of $\underline{q}'$.

We have concluded that we must express the right-hand side of Equation (2.35) to first order in a perturbation expansion in the pseudopotential. We were led to this conclusion by the necessity of obtaining a finite set of equations to solve for the matrix elements of V^{sc} and the desire to obtain an expression for $\langle \underline{q}|V^{sc}|0\rangle$ which depended upon $F(\underline{q}')$ only for $\underline{q}' = \underline{q}$. We should now ask how seriously we will limit the results of our theory by being able to calculate V^{sc} only to first order in the pseudopotential, W. This question is best answered after obtaining the form in which the matrix elements of the pseudopotential enter into the screening potential matrix elements. Proceeding with the calculation of the screening, we will associate the state $\bar{v}$ with the point $\underline{k}$ in reciprocal space. In other words, we will associate the zero'th order wavefunction, $a_o(\underline{k})\ |\underline{k}\rangle$, with $\bar{v}$ and calculate the perturbing effect of the pseudopotential on that initial state. This implies no more than a one-to-one correspondence between a listing of states according to v or $\bar{v}$ and a listing

according to $\underline{k}$. Specifically, it does not imply that $\underline{k}$ is a good quantum number in our system. If we expand the wave function $\bar{v}$ in terms of plane waves and neglect all terms higher than first order in the pseudopotential in a perturbation expansion of the coefficients of the plane waves, we can write

$$|\bar{v}\rangle = a_o(\underline{k})\ |\underline{k}\rangle + \Sigma'_{\{\underline{q}\}}\ a_q(\underline{k})\ |\underline{k}+\underline{q}\rangle\ , \tag{2.40}$$

where

$$a_q(\underline{k}) = \frac{a_o(\underline{k})\ \langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2}\ , \qquad q \neq 0\ . \tag{2.41}$$

The primed sum in Equation (2.40) is over all the members of $\{\underline{k}\}$ except $\underline{q} = 0$. The first order Expression (2.41) results from a standard perturbation theory expansion in the pseudopotential [2] once we recall that the eigenvalue of T operating on the plane wave $\underline{k+q}$ is $(|\underline{k+q}|^2 + \bar{V}_L)$. In writing Expression (2.41), we have neglected the vanishing of the denominator for certain values of $q \neq 0$. As we mentioned previously, a matrix element of the pseudopotential of a periodic crystal between two plane waves vanishes unless the wave vectors of the plane waves differ by a member of the set $\{\underline{K}_s\}$. Then for those values of $\underline{k}$ such that $|\underline{k}|^2 = |\underline{k+K_s}|^2$, Expression (2.41) diverges for a periodic crystal. The effect of the higher orders of perturbation theory is no longer small and we say that perturbation theory breaks down. This corresponds to a Bragg reflection of the plane wave $\underline{k}$ and the occurrence of a band gap in the energy spectrum. For an alloy which is

not in an ordered state, none of the matrix elements of the pseudopotential vanish identically. Therefore, for each value of $\underline{k}$, Equation (2.41) will diverge for a set of values of $\underline{q}$ lying on a sphere in reciprocal space.

Since the pseudopotential enters into the screening only through Equation (2.40), and we are going to drop all terms on the right-hand side of Equation (2.35) which are higher than first-order in the pseudopotential, the screening will only depend upon the sum of terms like Expression (2.41) over all values of $\underline{k}$ within the Fermi sphere,

$$\Sigma_{(\underline{k})_F} \frac{\langle \underline{k}+\underline{q}|W|\underline{k}\rangle \; g(\underline{k})}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \tag{2.42}$$

The function $g(\underline{k})$ has been inserted into the above sum to account for any $\underline{k}$ dependent factor which might be multiplied by Expression (2.41). As the size of crystal increases arbitrarily at constant ionic volume, the values of $\underline{k}$ become arbitrarily close together and the sum in Expression (2.42) becomes arbitrarily close to an integral. Since the numerator in Expression (2.42) is going to be slowly varying in the vicinity of the divergence associated with the denominator, the integrand behaves like $1/x$ through the divergence. The principal value of such an integral is perfectly well-defined as long as the boundary of the integration is not arbitrarily close to $x = 0$ [5]. Therefore, the value of Expression (2.42) may be a small number even though there are values of $\underline{k}$ for which the integrand diverges. If this is indeed the case, perturbation theory to first order in the pseudopotential does suffice to

express the screening potential fairly accurately, even though it does not express individual terms in Expression (2.42) accurately. However, the divergence of the integrand in Expression (2.42) can give rise to a band gap. Thus, a system might certainly exist where the screening potential might be quite well approximated by first-order perturbation theory, yet we might be forced to solve a secular matrix equation to calculate the electronic energy at particular points in reciprocal space. This would not be inconsistent in any way. The approximation of first-order screening does not restrict us in any direct way to a consistent treatment of electron energies to some particular order in perturbation theory. We must consider ascertaining the validity of first-order screening as a problem separate from ascertaining the validity of using second-order perturbation theory to approximate the electron energies.

We might note that there are certain interesting physical cases where the calculation of the screening potential to first-order in the pseudopotential is a poor approximation, and where integrals like Expression (2.42) might even diverge. Let us consider the case where the Fermi surface is tangent, or nearly tangent, to a plane in reciprocal space where one might expect a band gap. Then an integral over the Fermi sphere, such as Expression (2.42), will have large contributions from points on the low energy side of the band gap with no compensating contributions of opposite sign from points on the high energy side of the band gap. Under these conditions, Expression (2.42) will have a

large, if not arbitrarily large, value and first-order perturbation theory will not suffice to express the matrix elements of V^{sc}. The stability of certain long period super-lattices in alloy systems is believed to depend upon the Fermi surface being tangent to such a plane in reciprocal space. Such systems are therefore not amenable to the treatment of the screening which was described above. According we could not separate the matrix elements of the pseudopotential in such systems as we wish to do. As we shall see in the next chapter, this would prevent us from expressing the total electronic energy of the system in terms of a two-particle correlation function. The ability to well approximate the screening using first-order perturbation theory is therefore central to the results of this work. We shall proceed formally as though there were no divergence in Expression (2.41), but we must ascertain the validity of this treatment in particular cases.

If we substitute Equations (2.40) and (2.41) into Equation (2.36), we may write the wave density, $\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle$, to first order in the pseudopotential as

$$\begin{aligned}\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle = |a_0(\underline{k})|^2 \Big[& \langle \underline{r}|\underline{k}\rangle\langle \underline{k}|\underline{r}\rangle - 2\mathrm{RE}\, \Sigma_c \langle \underline{r}|c\rangle\langle c|\underline{k}\rangle\langle \underline{k}|\underline{r}\rangle \\ & + \Sigma_c\, \Sigma_{c'} \langle \underline{r}|c\rangle\langle c|\underline{k}\rangle\langle \underline{k}|c'\rangle\langle c'|\underline{r}\rangle \Big] \\ + 2|a_0(\underline{k})|^2\, \mathrm{RE}\, \Sigma'_{\{\underline{q}\}} & \frac{\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \\ & \times \Big[\langle \underline{r}|\underline{k}+\underline{q}\rangle\langle \underline{k}|\underline{r}\rangle - \Sigma_c \langle \underline{r}|c\rangle\langle c|\underline{k}+\underline{q}\rangle\langle \underline{k}|\underline{r}\rangle \\ & \quad - \Sigma_c \langle \underline{r}|\underline{k}+\underline{q}\rangle\langle \underline{k}|c\rangle\langle c|\underline{r}\rangle \\ & \quad + \Sigma_{c,c'} \langle \underline{r}|c\rangle\langle c|\underline{k}+\underline{q}\rangle\langle \underline{k}|c'\rangle\langle c'|\underline{r}\rangle \Big] \quad . \end{aligned} \tag{2.43}$$

The integral of Expressions (2.43) over the entire crystal should be unity since the state v contains just one electron. This yields an expression for $|a_o(\underline{k})|^2$ as follows:

$$|a_o(\underline{k})|^2 = \left\{1 - \Sigma_c\langle\underline{k}|c\rangle\langle c|\underline{k}\rangle - 2\mathrm{RE}\,\Sigma'_{\{\underline{q}\}}\frac{\langle\underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2}\left[\Sigma_c\langle\underline{k}|c\rangle\langle c|\underline{k}+\underline{q}\rangle\right]\right\}^{-1}, \qquad (2.44)$$

where we have used the orthogonality of the core states of H. We are also interested in the matrix elements of Equation (2.43) between plane waves $\underline{q}$ and 0, which we will wish to insert into the right-hand side of Equation (2.35). To first order in the pseudopotential, the matrix elements of the charge density associated with the state v are given by

$$\begin{aligned}\langle\underline{q}|[\langle\underline{r}|v\rangle\langle v|\underline{r}\rangle]|0\rangle = {}& \frac{|a_o(\underline{k})|^2}{\Omega}\Big[-\Sigma_c[\langle\underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle+\langle\underline{k}|c\rangle\langle c|\underline{k}-\underline{q}\rangle] \\ &+\Sigma_c\Sigma_{c'}\langle\underline{k}|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle\Big] \\ &+\frac{|a_o(\underline{k})|^2}{\Omega}\left\{\frac{\langle\underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2}+\frac{\langle\underline{k}-\underline{q}|W|\underline{k}\rangle^*}{|\underline{k}|^2-|\underline{k}-\underline{q}|^2}\right\} \\ &+\frac{|a_o(\underline{k})|^2}{\Omega}\Sigma'_{\{\underline{q}'\}}\frac{\langle\underline{k}+\underline{q}'|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}'|^2}\Big[+\Sigma_{c,c'}\langle\underline{k}|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}+\underline{q}'\rangle \\ &\qquad -\Sigma_c[\langle\underline{k}+\underline{q}|c\rangle\langle c|\underline{k}+\underline{q}'\rangle+\langle\underline{k}|c\rangle\langle c|\underline{k}+\underline{q}'-\underline{q}\rangle]\Big] \\ &+\frac{|a_o(\underline{k})|^2}{\Omega}\Sigma'_{\{\underline{q}'\}}\frac{\langle\underline{k}+\underline{q}'|W|\underline{k}\rangle^*}{|\underline{k}|^2-|\underline{k}+\underline{q}'|^2}\Big[+\Sigma_{c,c'}\langle\underline{k}+\underline{q}'|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle \\ &\qquad -\Sigma_c[\langle\underline{k}+\underline{q}'|c\rangle\langle c|\underline{k}-\underline{q}\rangle+\langle\underline{k}+\underline{q}'+\underline{q}|c\rangle\langle c|\underline{k}\rangle]\Big]. \qquad (2.45)\end{aligned}$$

In order to more fully understand the implications of Equations (2.44) and (2.45), we must investigate the nature of the sums over c which are involved. Let us first consider the sum which occurs in Equation (2.44)

$$\Sigma_c \langle \underline{k} + q | c \rangle \langle c | \underline{k} \rangle \ . \tag{2.46}$$

We may fully express the sums involved in Expression (2.46) as

$$\Sigma_{\{\underline{R}\}} \Sigma_{nlms} \langle \underline{k} + \underline{q} | nlms; \underline{R} \rangle \langle nlms; \underline{R} | \underline{k} \rangle \ . \tag{2.47}$$

Since the core wavefunctions associated with a particular element have been assumed to be independent of the local environment of the core in the crystal, we may separate Expression (2.47) in a manner analogous to the separation of Expression (2.19). In order to simplify our notation, let us define a projection operator associated with the core states of an ion of type i located at $\underline{R}$ by

$$P_i(\underline{r} - \underline{R}, \underline{r}' - \underline{R}) \equiv \Sigma_{nlms} \langle \underline{r} - \underline{R} | nlms; i \rangle \langle nlms; i | \underline{r}' - \underline{R} \rangle \ . \tag{2.48}$$

From the invariance of the core states, we may use this definition to write Expression (2.46) as

$$\Sigma_c \langle \underline{k} + \underline{q} | c \rangle \langle c | \underline{k} \rangle = \frac{1}{2} \Sigma_{\{\underline{R}\}} \langle \underline{k} + \underline{q} | \{ (1 + \sigma(\underline{R})) \ P_A(\underline{r} - \underline{R}, \underline{r}' - \underline{R}) + (1 - \sigma(\underline{R})) \ P_B(\underline{r} - \underline{R}, \underline{r}' - \underline{R}) \} | \underline{k} \rangle . \tag{2.49}$$

In computing the matrix elements of P_A and P_B in Equation (2.49), we may translate the origins of our integrations to the points $\underline{R}$ and rewrite as

$$\Sigma_c \langle \underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle = \frac{1}{2}\Sigma_{\{\underline{R}\}}\left\{\frac{(1+\sigma(\underline{R}))}{N} e^{-i\underline{q}\cdot\underline{R}} \langle \underline{k}+\underline{q}|P_A|\underline{k}\rangle_{\Omega_o} + \frac{(1-\sigma(\underline{R}))}{N} e^{-i\underline{q}\cdot\underline{R}} \langle \underline{k}+\underline{q}|P_B|\underline{k}\rangle_{\Omega_o}\right\}, \tag{2.50}$$

where

$$\langle \underline{k}+\underline{q}|P_i|\underline{k}\rangle_{\Omega_o} = \frac{1}{\Omega_o}\Sigma_{nlms}\int_\Omega d\underline{r}\int_\Omega d\underline{r}'\, e^{-i(\underline{k}+\underline{q})\cdot\underline{r}} \langle \underline{r}|nlms;i\rangle \times \langle nlms;i|\underline{r}'\rangle\, e^{i\underline{k}\cdot\underline{r}'} \tag{2.51}$$

In analogy with our previous separation of W^o, we may define an average projection operator,

$$\langle \underline{k}+\underline{q}|\bar{P}|\underline{k}\rangle \equiv x\langle \underline{k}+\underline{q}|P_A|\underline{k}\rangle_{\Omega_o} + (1-x)\langle \underline{k}+\underline{q}|P_B|\underline{k}\rangle_{\Omega_o}\,, \tag{2.52}$$

and a difference projection operator

$$\langle \underline{k}+\underline{q}|\Delta P|\underline{k}\rangle \equiv \tfrac{1}{2}\langle \underline{k}+\underline{q}|P_A|\underline{k}\rangle_{\Omega_o} - \tfrac{1}{2}\langle \underline{k}+\underline{q}|P_B|\underline{k}\rangle_{\Omega_o}\,. \tag{2.53}$$

These definitions may be coupled with our definition of $F(\underline{q})$ and our discussion of the Kronecker delta to write Expression (2.46) in the form of Equation (2.33),

$$\Sigma_c \langle \underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle = \delta_{\underline{q},\{\underline{K}\}}\langle \underline{k}+\underline{q}|\bar{P}|\underline{k}\rangle + F(\underline{q})\langle \underline{k}+\underline{q}|\Delta P|\underline{k}\rangle\,. \tag{2.54}$$

If we substitute from Equations (2.33) and (2.54) into that part of the last term of Equation (2.44) which is associated with W^o, we obtain a product of which one of the factors is

$$\Sigma'_{\{\underline{K}\}} \frac{\langle \underline{k}+\underline{K}|\bar{W}^c|\underline{k}\rangle\langle \underline{k}|\bar{P}|\underline{k}+\underline{K}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{K}|^2} + \Sigma'_{\{\underline{q}\}} \frac{|F(\underline{q})|^2\langle \underline{k}+\underline{q}|\Delta W^o|\underline{k}\rangle\langle \underline{k}|\Delta P|\underline{k}+\underline{q}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \tag{2.55}$$

Note that no cross products occur in Expression (2.55) because $\delta_{\underline{q},\{\underline{K}\}}F(\underline{q})$

is identically zero for all values of $\underline{q}$ as we observed in our discussion of Expressions (2.31) and (2.32). We may see from Expression (2.55) that an expression for $|a_o(\underline{k})|^2$ which is strictly first order in the pseudopotential would depend on $F(\underline{q}')$ for all values of $\underline{q}'$. As we discussed in deciding on the order in perturbation theory to which we could calculate V^{sc}, the presence of such a dependence on the right-hand side of Equation (2.35) would prevent us from separating the pseudopotential. We wish an expression for $\langle \underline{q}|V^{sc}|0\rangle$ which involves $F(\underline{q}')$ only for $\underline{q}' = \underline{q}$. Accordingly, we would like to drop the last part of Equation (2.44) from our expression for $|a_o(\underline{k})|^2$. Fortunately, calculations by Harrison [2] and others have shown that the sum in Expression (2.46) is usually on the order of 0.10, varying between rough limits of 0.05 and 0.22, for $\underline{q} = 0$. For a given $\underline{k}$, the sum is a slowly varying function of $\underline{q}$ which reaches its maximum in the vicinity of $\underline{q} = 0$. While we are reluctant to call such a sum a first-order expression in the pseudopotential, it is reasonable to compare its magnitude with that of an expression like

$$\frac{\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} . \tag{2.56}$$

A typical value for this factor might be that for $\underline{k} = 0$ and for $\underline{q}$ set equal to one-half of that reciprocal space vector of $\{\underline{K}\}$ which has the smallest magnitude. A survey of the pseudopotentials of the various single-element crystals which were listed by Harrison [2] indicates that a typical magnitude for Expression (2.56) might be 0.2,

with rough limits of 0.0 and 0.4. Expression (2.56) may be zero for particular values of $\underline{k}$ and $\underline{q}$ depending upon the pseudopotential used, but we feel that 0.2 is truly representative of its magnitude. Accordingly, we shall generalize and consider the sum in Expression (2.46) as being roughly comparable with a first order term in the pseudopotential. This approximation must be verified for particular systems.

With that approximation, we can write the expression for $|a_o(\underline{k})|^2$ to "first-order" in the pseudopotential as

$$|a_o(\underline{k})|^2 = [1 - \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle]^{-1} \tag{2.57}$$

Similarly, we may write Equation (2.45) to first order in the pseudopotential as

$$\langle \underline{q}|[\langle \underline{r}|v\rangle\langle v|\underline{r}\rangle]|0\rangle = \frac{|a_o(\underline{k})|^2}{\Omega}\Big[-\Sigma_c[\langle \underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle + \langle \underline{k}|c\rangle\langle c|\underline{k}-\underline{q}\rangle] + \Sigma_c\Sigma_{c'}\langle \underline{k}|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle\Big]$$
$$+ \frac{|a_o(\underline{k})|^2}{\Omega}\left\{\frac{\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} + \frac{\langle \underline{k}-\underline{q}|W|\underline{k}\rangle^*}{|\underline{k}|^2-|\underline{k}-\underline{q}|^2}\right\}, \tag{2.58}$$

once we observe that terms like

$$\Sigma_c\,\Sigma_{c'}\langle \underline{k}+\underline{q}'|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle\ , \tag{2.59}$$

may be considered as comparable with Equation (2.46). For $\underline{q} = 0$ in Expression (2.59), the orthogonality of the core states of H allows us to reduce that expression to Expression (2.46). The presence of $\exp(-i\underline{q}\cdot\underline{r})$ in the middle integral merely serves to spread out the sharp orthogonality condition and should not increase the magnitude

of Expression (2.59) above that of Expression (2.46). Expression (2.54) demonstrates that Expression (2.57) for $|a_o(\underline{k})|^2$ does not involve $F(\underline{q})$, since $\underline{q} = 0$ is a member of the set $\{\underline{K}\}$. Thus the dependence of the matrix elements of V^{sc} upon $F(\underline{q})$ must come from the two factors in braces in Equation (2.58). Let us define a function $B(\underline{k},\underline{q})$ as

$$B(\underline{k},\underline{q}) \equiv -\Sigma_c[\langle \underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle + \langle \underline{k}|c\rangle\langle c|\underline{k}-\underline{q}\rangle]$$
$$+\Sigma_c\, \Sigma_{c'} \langle \underline{k}|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle \ . \tag{2.60}$$

With this definition, we may rewrite Equation (2.58) and substitute it into the right-hand side of Equation (2.35) to obtain

$$\langle \underline{q}|V^{sc}|0\rangle = \frac{8\pi}{\Omega|\underline{q}|^2}\, \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \left\{ \frac{\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} + \frac{\langle \underline{k}-\underline{q}|W|\underline{k}\rangle^*}{|\underline{k}|^2-|\underline{k}-\underline{q}|^2} + B(\underline{k},\underline{q}) \right\} . \tag{2.61}$$

The sum over $\{\underline{k}\}_F$ is over all the values of $\underline{k}$ within the Fermivolume. If we recall that $W = W^o + V^{sc}$ and that $\langle \underline{k}+\underline{q}|V^{sc}|\underline{k}\rangle$ is independent of $\underline{k}$, we may solve for the matrix elements of the screening potential, V^{sc}, in terms of the unscreened pseudopotential. The expression for these matrix elements is

$$\langle \underline{q}|V^{sc}|0\rangle = \frac{8\pi}{\Omega|\underline{q}|^2 D(\underline{q})}\, \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \left\{ \frac{\langle \underline{k}+\underline{q}|W^o|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} + \frac{\langle \underline{k}-\underline{q}|W^o|\underline{k}\rangle^*}{|\underline{k}|^2-|\underline{k}-\underline{q}|^2} + B(\underline{k},\underline{q}) \right\} , \tag{2.62}$$

where

$$D(\underline{q}) \equiv 1 - \frac{8\pi}{\Omega|\underline{q}|^2}\, \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \left\{ \frac{1}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} + \frac{1}{|\underline{k}|^2-|\underline{k}-\underline{q}|^2} \right\} . \tag{2.63}$$

It is apparent from the form of Equation (2.62) and the separability of the matrix elements of W^o that the separability of V^{sc}, as discussed in connection with W^o, will follow directly from the separability of $B(\underline{k},\underline{q})$. Equation (2.54) demonstrates the separability of the first sum in Expression (2.60) for $B(\underline{k},\underline{q})$. We have already assumed that the core state wavefunctions may be well approximated in the solid by the corresponding atomic wavefunctions. This is a reasonable approximation only if the overlap of core wavefunctions on adjacent ions in the solid is negligible. Accordingly, the middle integral in the last term in Equation (2.60) must vanish unless c and c' are on the same ion. We may use this property and the definition of the core projection operator to write this last sum as

$$\begin{aligned}\Sigma_c\Sigma_{c'}\langle\underline{k}|c\rangle\langle c|e^{-i\underline{q}\cdot\underline{r}}|c'\rangle\langle c'|\underline{k}\rangle \\ = \tfrac{1}{2}\Sigma_{\{\underline{R}\}}\langle\underline{k}|\Big[(1+\sigma(\underline{R}))\int d\underline{r}'P_A(\underline{r}-\underline{R},\underline{r}'-\underline{R})\,e^{-i\underline{q}\cdot\underline{r}'}P_A(\underline{r}'-\underline{R},\underline{r}''-\underline{R}) \\ +(1-\sigma(\underline{R}))\int d\underline{r}'P_B(\underline{r}-\underline{R},\underline{r}'-\underline{R})\,e^{-i\underline{q}\cdot\underline{r}'}P_B(\underline{r}'-\underline{R},\underline{r}''-\underline{R})\Big]|\underline{k}\rangle\ .\end{aligned} \tag{2.64}$$

We may now follow the customary procedure of translating the origins of the integration coordinates to the point $\underline{R}$ and defining an average function,

$$\bar{b}(\underline{k},\underline{q}) = x\,b_A(\underline{k},\underline{q}) + (1-x)b_B(\underline{k},\underline{q})\ , \tag{2.65}$$

and a difference function,

$$\Delta b(\underline{k},\underline{q}) = \tfrac{1}{2}b_A(\underline{k},\underline{q}) - \tfrac{1}{2}b_B(\underline{k},\underline{q})\ , \tag{2.66}$$

where

$$b_i(\underline{k},\underline{q}) = -\langle \underline{k}+\underline{q}|P_i|\underline{k}\rangle_{\Omega_o} - \langle \underline{k}|P_i|\underline{k}-\underline{q}\rangle_{\Omega_o}$$
$$+ N \sum_{\substack{nlms \\ n'l'm's'}} \langle \underline{k}|nlms;i\rangle \left[\int d\underline{r} \langle nlms;i|\underline{r}\rangle e^{-i\underline{q}\cdot\underline{r}}\right.$$
$$\left. \times \langle \underline{r}|n'l'm's';i\rangle\right] \langle n'l'm's';i|\underline{k}\rangle \quad . \tag{2.67}$$

We may now express $B(\underline{k},\underline{q})$ in separated form as

$$B(\underline{k},\underline{q}) = \delta_{\underline{q},\{\underline{K}\}}\bar{b}(\underline{k},\underline{q}) + F(\underline{q})\Delta b(\underline{k},\underline{q}) \quad . \tag{2.68}$$

Returning to Equation (2.62), we observe that, for $\underline{q}$ equal to some member of the set $\{\underline{K}\}$, the matrix element of V^{sc} involves only the average quantities. Similarly, for all other values of $\underline{q}$, the matrix element of V^{sc} involves only the difference quantities. Therefore, we may quite naturally separate the matrix elements of V^{sc} as we did the matrix elements of W^o. If we define an average screening potential,

$$\langle \underline{q}|\bar{v}^{sc}|0\rangle = \frac{8\pi}{\Omega|\underline{q}|^2 D(\underline{q})} \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \left\{ \frac{\langle \underline{k}+\underline{q}|\bar{w}^o|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} + \frac{\langle \underline{k}-\underline{q}|\bar{w}^o|\underline{k}\rangle^*}{|\underline{k}|^2 - |\underline{k}-\underline{q}|^2} + \bar{b}(\underline{k},\underline{q}) \right\} , \tag{2.69}$$

and a difference screening potential,

$$\langle \underline{q}|\Delta v^{sc}|0\rangle = \frac{8\pi}{\Omega|\underline{q}|^2 D(\underline{q})} \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \left\{ \frac{\langle \underline{k}+\underline{q}|\Delta w^o|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} + \frac{\langle \underline{k}-\underline{q}|\Delta w^o|\underline{k}\rangle^*}{|\underline{k}|^2 - |\underline{k}-\underline{q}|^2} + \Delta b(\underline{k},\underline{q}) \right\} , \tag{2.70}$$

we can write the matrix elements of the screening potential as

$$\langle \underline{q}|V^{sc}|0\rangle = \delta_{\underline{q},\{\underline{K}\}}\langle \underline{q}|\bar{v}^{sc}|0\rangle + F(\underline{q})\langle \underline{q}|\Delta v^{sc}|0\rangle \quad . \tag{2.71}$$

We might stop at this point and compare the results of this theory with the results of Harrison [6] for a single element crystal. As we noted before, the difference potential would vanish for a single-element crystal. We would expect that the single-element screening potential would be given essentially by Equation (2.69) in the limit as the two types of ionic potentials become equal. However, we can obtain Harrison's expression for the screening from Equation (2.69) only if we set $|a_o(\underline{k})|^2 = 1$ and $\bar{b}(\underline{k},\underline{q}) = 0$.* In agreement with our approximation the "order" of Expression (2.46), we might argue that setting $|a_o(\underline{k})|^2 = 1$ does not drop any terms from Equation (2.69) which are not second or higher order in the pseudopotential. However, $\bar{b}(\underline{k},\underline{q})$ should be considered as comparable with a truly first-order contribution to the pseudopotential. For the system which we have chosen as an example, the factor $|a_o(\underline{k})|^2$ increases the matrix elements of the screening potential by six to eight per cent for important values of $\underline{q}$. Similarly, the terms $\bar{b}(\underline{k},\underline{q})$ and $\Delta b\,(\underline{k},\underline{q})$ decrease the screening potential matrix elements by about one per cent for $\underline{q} = 0.25$ atomic units (a.u.) and by about forty per cent for $\underline{q} = 1.50$ a.u. Thus, the combined effect of the two corrections tends to redistribute the screening effects in $\underline{q}$-space. The effects tend to cancel to a certain extent and we have accordingly included both of them in our formalism. The effect of these corrections on the screened pseudopotential is much more dramatic for small values of $\underline{q}$ since the screening potential and the unscreened pseudopotential cancel to a large extent in this region. We conclude

*Harrison has included some of the effects of these terms in his concept of effective valence.

that these effects should be included in an accurate screening calculation for either a single-element crystal or an alloy. Proceeding accordingly, we wish to add our V^{sc} to W^{o} to obtain the screened pseudopotential. Equations (2.33) and (2.71) allow us to write the matrix elements of the total screened pseudopotential as

$$\langle \underline{k}+\underline{g}|W|\underline{k}\rangle = \sum_{\{\underline{K}\}} \langle \underline{k}+\underline{g}|\bar{W}|\underline{k}\rangle + F(\underline{g})\langle \underline{k}+\underline{g}|\Delta W|\underline{k}\rangle \ , \tag{2.72}$$

where $\bar{W} = \bar{W}^{o} + \bar{V}^{sc}$ and $\Delta W = \Delta W^{o} + \Delta V^{sc}$.

Since we have succeeded in our aim of separating the full pseudopotential in the sense discussed in connection with Expressions (2.31) and (2.32), we shall review the assumptions which were required to achieve this separation. Starting with the Austin, Heine, and Sham form of the pseudopotential, we first assumed that the core eigenfunctions did not depend upon the local environment of the ion and that we could use the corresponding atomic wavefunctions in their places. Later we made use of the implication of this invariance that the core eigenfunctions on adjacent ions in the solid did not overlap. We assumed that a Hartree-Fock one-electron Hamiltonian was sufficient to describe the interaction of the conduction electron eigenstates with the core electron eigenstates. These assumptions are common to all OPW and pseudopotential approaches. Then we restricted the form which we might finally choose for $f_c(\underline{r})$ to one which did not vary among the ions of one type throughout the alloy, for a particular configuration of ions.

These assumptions and the restriction on $f_c(\underline{r})$ allowed us to separate the unscreened pseudopotential into the form of Equation (2.33). The matrix elements of $\bar{w}^o$ and Δw^o, however, depend upon the configuration of the ions to the extent that we allow the chosen form of $f_c(\underline{r})$ to depend on the configuration. Approximating the electronic potential with a Hartree potential, we found that we could not separate V^{sc} unless we calculated the screening potential matrix elements only to first order in the pseudopotential using a perturbation expansion. This approximation was also necessitated to a large extent by our inability to solve a set of N dependent equations. As we discussed at the time, this approximation for V^{sc} does not restrict us to calculating the electron energies to some particular order in the pseudopotential. At points corresponding to band gaps, the approximation we have used to obtain V^{sc} should not stop us from diagonalizing some limited matrix to obtain the eigenvalues. This is because the accuracy of the matrix elements of V^{sc} depends upon some average over the Fermi sphere of the error in a first order perturbation theory treatment of the electronic eigenfunctions, and consequently may not be greatly affected by the band gaps in particular instances. Further, we found it necessary for the separation of V^{sc} to consider terms like Expression (2.46) as first order in the pseudopotential. An examination of typical magnitudes demonstrated the validity of this assumption. Finally, we were able to separate the screened pseudopotential into the form shown in Equation (2.72).

The Ordering Energy and the Pairwise Interactions

Our derivation of the form of the screened pseudopotential was motivated by a desire to calculate the total conduction electron energy and the electronic contribution to the ordering energy of an alloy. We also wish to use the form of the ordering energy to deduce an expression for the effective pairwise interactions. In order to facilitate our discussion of the total energy of the system, we will distinguish two separate groups of charges in the crystal. One group consists of the ionic cores, composed of the nucleii and the core electrons on all the sites in the crystal. The second group consists of all that charge associated with the occupied valence states of H, including the uniform charge distribution, the screening charge density, and that charge which has been associated with the cores through the action of projection operators such as $\Sigma_c \langle \underline{r}|c\rangle\langle c|\underline{r}\rangle$ in Equation (2.15). In other treatments [6], the uniform distribution and the screening charge density are associated with the charge density of the occupied states of $\bar{v}$. The conduction electron charge which has been associated with the cores by the projection operator is then combined with the charge on the ionic cores to yield an effective valence. For our purposes, however, the division of charges mentioned earlier is more convenient.

We have assumed that the wavefunctions of the core electrons may be approximated well by the corresponding atomic wavefunctions. Therefore, we are neglecting the van der Waal's interactions among the cores.

We are also neglecting any interactions which may arise due to a slight overlap of the charge densities associated with adjacent cores. Accordingly, the energy of the first group of charges is simply that of a collection of point charges. If there are Z_i positive charges associated with each ion of type i, then we may use the the function $\sigma(\underline{R})$ to write the self energy per ion of the first group of charges as

$$\frac{1}{2N} \Sigma_{\{\underline{R}\}} \Sigma_{\{\underline{R}'\}} \frac{2}{|\underline{R} - \underline{R}'|} \left\{ \left[\frac{(1 + \sigma(\underline{R}))}{2} Z_A + \frac{(1 - \sigma(\underline{R}))}{2} Z_B \right] \times \left[\frac{(1 + \sigma(\underline{R}'))}{2} Z_A + \frac{(1 - \sigma(\underline{R}'))}{2} Z_B \right] \right\} . \qquad (2.73)$$

The total energy of the crystal includes the contribution of Expression (2.73), the self-energy of the second group of charges, and the energy of interaction between the two groups. If we sum the electronic eigenvalues, E_v, over all of the occupied valence states of H, we will obtain the total kinetic energy of the electrons plus the energy of interaction of the second group of charges with both the first and the second groups of charges. This sum correctly accounts for the energy of interaction between the two groups, but counts the Hartree self-energy of the second group of charges twice. Therefore, the contribution of the conduction electrons to the total energy of the crystal is given by the sum of E_v over all of the occupied states less the self-energy of the conduction electron charge density in the Hartree approximation. We may let E_v be denoted by $E_{\underline{k}}$ and perform the sum over all the points in the Fermi volume. If we let the conduction electron

charge density be denoted by $n_{CE}(\underline{r})$, we may write the conduction electron contribution to the total energy per ion as

$$\frac{1}{N}\Sigma_{\{\underline{k}\}_F} E_{\underline{k}} - \frac{1}{N}\int d\underline{r}\int d\underline{r}' \frac{n_{CE}(\underline{r})\, n_{CE}(\underline{r}')}{|\underline{r}-\underline{r}'|} . \tag{2.74}$$

In order to discuss the second term in Expression (2.74), we will expand the density of the conduction electrons in terms of its Fourier components using

$$n_{CE}(\underline{r}) = n_o + \Sigma'_{\{\underline{q}\}} n_{\underline{q}}\, e^{i\underline{q}\cdot\underline{r}} . \tag{2.75}$$

Now let us examine the contribution to Expression (2.74) of the constant part of $n_{CE}(\underline{r})$ interacting with the spatially varying part of $n_{CE}(\underline{r}')$. We may write this contribution as

$$-\frac{1}{N}\Sigma'_{\{\underline{q}\}} n_{\underline{q}} \int d\underline{r}\int d\underline{r}' \frac{n_o e^{i\underline{q}\cdot\underline{r}'}}{|\underline{r}-\underline{r}'|} . \tag{2.76}$$

Performing the integral over $\underline{r}'$, we may write Expression (2.76) as

$$-\frac{1}{N}\Sigma'_{\{\underline{q}\}} n_{\underline{q}}\, n_o \frac{2\pi}{|\underline{q}|^2}\int d\underline{r}\, e^{i\underline{q}\cdot\underline{r}} . \tag{2.77}$$

This expression vanishes since the integral over $\underline{r}$ is zero unless $\underline{q} = 0$, and we are excluding the term corresponding to $\underline{q} = 0$ from our sum over $\{\underline{q}\}$. Accordingly, there is no energy of interaction between the uniform and the spatially varying parts of the conduction electron charge density. We may repeat the above procedure to calculate the energy of interaction between the spatially varying part of $n_{CE}(\underline{r})$ and the spatially varying part of $n_{CE}(\underline{r}')$. Performing the integrations over $\underline{r}$ and $\underline{r}'$, we may express this energy as

$$- \frac{\Omega}{N} \Sigma'_{(\underline{q})} \frac{4\pi}{|\underline{q}|^2} n_{\underline{q}} n_{-\underline{q}} \quad . \tag{2.78}$$

But we may express Poisson's equation as given by Equation (2.34) in terms of $n_{\underline{q}}$ by

$$\langle \underline{q} | V^{sc} | 0 \rangle = \frac{8\pi}{|\underline{q}|^2} n_{\underline{q}} \quad . \tag{2.79}$$

We may substitute Expressions (2.78) and (2.79) into Expressions (2.74) to write the contribution of the conduction electrons to the total energy per ion of the crystal as

$$\frac{1}{N} \Sigma_{(\underline{k})_F} \mathcal{E}_{\underline{k}} - \frac{\Omega_o}{16\pi} \Sigma'_{(\underline{q})} |\underline{q}|^2 |\langle \underline{q} | V^{sc} | 0 \rangle|^2 - \frac{1}{N} \int d\underline{r} \int d\underline{r}' \frac{(n_o)^2}{|\underline{r} - \underline{r}'|} \quad . \tag{2.80}$$

The total energy of the crystal consists of the contributions which we have included in Expressions (2.73) and (2.80) added to the internal energy of the ions.

We should note at this point that some of the expressions which we have written down are divergent. The Coulomb sum and integrals which occur in Expressions (2.73) and (2.80) cannot be evaluated unless they are taken together. Accordingly, we will group the contributions to the total energy per ion so that each group has a finite energy. In the first group, we will include most of those terms which do not change when the ions are rearranged at constant volume. The first contribution to this group is the energy of an array of charges $\bar{Z}$ on each of the ionic sites in the crystal. If x is the fraction of ions of element A in the crystal, we may define $\bar{Z} \equiv x Z_A + (1 - x) Z_B$ in

analogy with our definition of the average pseudopotential. To this we will add the interaction of the uniform conduction electron density, n_o, with the potential due to the ions and electrons in the crystal. An average charge density interacts only with an average potential. For convenience, we will consider in the first group of energy contributions only the interaction of n_o with $\bar{V}_L$, which we have already defined as the spatial average of the potential due to the nucleii plus the spatial average of the Hartree potentials due to the core and conduction electrons. The interaction of n_o with the exchange potential of the cores will be included in the second group. Finally, since we have counted the self-energy of the uniform electron distribution twice, we must subtract it from the above contributions to obtain

$$\frac{1}{N} \Sigma_{\{\underline{R}\}\neq}\Sigma_{\{\underline{R}'\}} \frac{\bar{Z}^2}{|\underline{R}-\underline{R}'|} - n_o\bar{V}_L\Omega_o - \frac{(n_o)^2}{N} \int d\underline{r} \int d\underline{r}' \frac{1}{|\underline{r}-\underline{r}'|} + V^{II} . \quad (2.81)$$

We have included V^{II}, which is the internal energy of the ions. We would not expect V^{II} to change during changes in the configuration of the ions at constant volume since we have assumed that the core electron wavefunctions are always the corresponding atomic wavefunctions. With the exception of V^{II}, Expression (2.81) is essentially the Madelung energy of an array of equal positive charges in a uniform compensating density of electrons, and is accordingly a finite energy. We shall now turn to the remaining part of the total energy per ion.

In order to display the dependence of this second group of energy contributions on the pseudopotential, we must obtain an explicit expression for the electronic eigenvalues which occur in the first sum in Expression (2.80). When we first introduced the use of perturbation theory in connection with the calculation of the screening potential, we noted that certain terms in the expressions for the electronic energies and wavefunctions are undefined in the breakdown of perturbation theory associated with band gaps. Later, we noted that, in many instances, the integration of these expressions over the regions of divergence yields a well-defined result if one takes the principal part of the integral. We would accordingly like to use perturbation theory to second order in the pseudopotential to express the electronic eigenvalues. Since the integrands involved in the second-order perturbation theory expression for the total electronic energy are very similar to those involved in the first-order expression for the screening potential, we would expect that the accuracy of one approximation would be very closely related to the accuracy of the other. Therefore, if we may reasonably make the first approximation, regarding first-order screening, we may have some confidence that the total electronic energy may be approximated well by second-order perturbation theory. As we shall see shortly, both our expressions for the effective pairwise interactions and our ability to express the total electronic energy of the system in terms of a two-particle correlation function depend directly on the ability to make these two approximations. On the other hand, if we cannot make these approximations for some system, as we discussed in connection with the screening potential, then

neither of these results follow for this system. We cannot overemphasize the central nature of these approximations to the results of this work. We might mention in this connection the work of W. Kohn and C. Majumdar [9]. They have examined the behavior of a gas of independent fermions in the presence of an attractive localized potential. If the strength of the potential is gradually increased from a very small value, a fermion state will eventually undergo a transition to a bound state in the potential well. Kohn and Majumdar have shown that this transition produces no discontinuities in the properties of the system as a whole. By analogy, we would not expect that the band gaps introduced by the periodicity of a crystal would produce a discontinuous change in the properties of that crystal. Accordingly, we have reason to believe that the perturbation theory approximations regarding the screening and the total electronic energy will be good approximations except in special cases such as those we discussed in connection with the screening.

In light of this discussion, we shall express the electronic eigenvalues appearing in Expression (2.80) using second-order perturbation theory in the pseudopotential. We shall treat the terms involved as being well-defined everywhere since they appear only in integrations over the Fermi sphere, as in the case of the screening potential. We must remember that this is merely a formal result and that the accuracy of the total electronic energy must be verified in particular instances. To second-order in the pseudopotential, the electronic energies are given by

$$E_{\underline{k}} = |\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|W|\underline{k}\rangle + \Sigma'_{\{\underline{q}\}} \frac{\langle \underline{k}|W|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \quad . \tag{2.82}$$

The sum of the second term in Equation (2.82) over all points within the Fermi volume is just the energy of interaction of n_o with $\bar{V}_L$ and has already been included in Expression (2.81). We may now write that part of the total energy per ion of the crystal which was not included in Expression (2.81) as

$$\begin{aligned}
&\frac{1}{N}\Sigma_{\{\underline{R}\}}\sum_{\neq\{\underline{R}'\}} \frac{1}{|\underline{R}-\underline{R}'|}\left\{-\bar{Z}^2 + \left[\frac{(1+\sigma(\underline{R}))}{2} Z_A + \frac{(1-\sigma(\underline{R}))}{2} Z_B\right]\right. \\
&\qquad\qquad \left. \times \left[\frac{(1+\sigma(\underline{R}'))}{2} Z_A + \frac{(1-\sigma(\underline{R}'))}{2} Z_B\right]\right\} \\
&+ \frac{1}{N}\Sigma_{\{\underline{k}\}_F}\Sigma'_{\{\underline{q}\}} \frac{\langle \underline{k}|W|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} - \frac{\Omega_o}{16\pi}\Sigma'_{\{\underline{q}\}}|\underline{q}|^2|\langle \underline{q}|V^{sc}|0\rangle|^2 \\
&+ \frac{1}{N}\Sigma_{\{\underline{k}\}_F}\{|\underline{k}|^2 + \langle \underline{k}|W|\underline{k}\rangle\} \quad .
\end{aligned} \tag{2.83}$$

The ordering energy of the crystal is now the difference between Expression (2.83) evaluated in the ordered state and evaluated in the disordered state. Harrison [5] has shown that the contribution of the sum $E_{\underline{k}}$ over all points within the Fermi volume is given to second order in the pseudopotential by a sum of Expression (2.82) over all points in the Fermi sphere. Therefore, the last sum in Expression (2.83) changes during rearrangements of the ions at constant volume only through the dependence of W on $f_c(\underline{r})$. The electronic contribution to the ordering energy may be best expressed by defining energy-wavenumber characteristics appropriate to the alloy problem. Accordingly, we will define $E_{ij}(\underline{q})$ by

$$F_{ij}(\underline{q}) = \frac{1}{N} \Sigma_{\{\underline{k}\}_F} \frac{\langle \underline{k}|w_i|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|w_j|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} - \frac{\Omega_o|\underline{q}|^2}{16\pi} \langle 0|v_i|\underline{q}\rangle\langle \underline{q}|v_j|0\rangle \ , \tag{2.84}$$

where i and j may take on the values 1 and 2. In this notation, we shall let $w_1 = \bar{w}$, $w_2 = \Delta w$, $v_1 = \bar{v}^{sc}$, and $v_2 = \Delta v^{sc}$. From Expression (2.83), we may write that part of the conduction electronic energy which might contribute to the ordering process as

$$\frac{1}{N} \Sigma_{\{\underline{k}\}_F} \langle \underline{k}|W|\underline{k}\rangle$$

$$+ \frac{1}{N} \Sigma'_{\{\underline{q}\}} \left\{ \Sigma_{\{\underline{k}\}_F} \frac{\langle \underline{k}|W|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} - \frac{\Omega|\underline{q}|^2}{16\pi} |\langle 0|V^{sc}|\underline{q}\rangle|^2 \right\} . \tag{2.85}$$

We may now insert the expressions for the matrix elements of W and V^{sc} given by Equations (2.71) and (2.72). Since either $F(\underline{q})$ or the Kronecker delta will always vanish for a given value of $\underline{q}$, there will be no terms in Expression (2.85) arising from products of average and difference potentials. Accordingly, we may write Expression (2.85) as

$$\frac{1}{N} \Sigma_{\{\underline{k}\}_F} \langle \underline{k}|\bar{w}|\underline{k}\rangle + \Sigma'_{\{\underline{q}\}} \{\delta_{\underline{q},\{\underline{K}\}} E_{11}(\underline{q}) + |F(\underline{q})|^2 E_{22}(\underline{q})\} \ . \tag{2.86}$$

The change of Expression (2.86) between the ordered and the disordered states accounts for the conduction electron contribution to the ordering energy. We have retained the terms involving the average potentials since these will vary if $f_c(\underline{r})$ is allowed to vary between the ordered and disordered states. If we restrict $f_c(\underline{r})$ so that it is invariant during rearrangements of the ions at constant volume, then the conduction

electron contribution to the ordering energy will depend upon those terms involving the difference potentials, as one might expect.

Having derived an expression for the conduction electron contribution to the ordering energy, we turn now to the effective pairwise interactions. Returning to Expression (2.85), we will again substitute Equations (2.71) and (2.72) for the matrix elements of W and V^{sc}. Instead of using the special properties of $F(\underline{q})$ and the Kronecker delta, we will express them in terms of their sums in real space, as in Equations (2.31) and (2.32). We may take these two sums outside of the sums over $\{\underline{k}\}_F$ and $\{\underline{q}\}$ in Expression (2.85) to obtain

$$\frac{1}{N}\Sigma_{\{\underline{k}\}_F}\langle\underline{k}|\bar{w}|\underline{k}\rangle + \frac{1}{2N}\Sigma_{\{\underline{R}\}}\Sigma_{\{\underline{R}'\}}\frac{2}{N}\Sigma'_{\{\underline{q}\}}e^{i\underline{q}\cdot(\underline{R}-\underline{R}')}\Big[E_{11}(\underline{q}) + (\sigma(\underline{R}') - \langle\sigma\rangle_{\underline{R}})E_{12}(\underline{q}) + (\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})E_{21}(\underline{q}) + (\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})(\sigma(\underline{R}') - \langle\sigma\rangle_{\underline{R}})E_{22}(\underline{q})\Big] . \qquad (2.87)$$

By analogy with the form of Expression (2.73), we see that the energy of interaction by means of the conduction electrons between an ion of element A at $\underline{R}$ and another ion of element A at $\underline{R}'$ is just given by substituting $\sigma(\underline{R}) = \sigma(\underline{R}') = 1$ into the appropriate term in Expression (2.87) to obtain

$$\frac{2}{N}\Sigma'_{\{\underline{q}\}}e^{i\underline{q}\cdot(\underline{R}-\underline{R}')}\{E_{11}(\underline{q}) + (1 - \langle\sigma\rangle_{\underline{R}})(E_{12}(\underline{q}) + E_{21}(\underline{q})) + (1 - \langle\sigma\rangle_{\underline{R}})^2 E_{22}(\underline{q})\} \qquad (2.88)$$

Recall that the energy-wavenumber characteristics depend on $f_c(\underline{r})$ through the pseudopotential. Therefore, we find that we must restrict $f_c(\underline{r})$ so that it does not vary during rearrangements of the ions at constant volume in order to obtain an indirect interaction which does not depend upon the state of order. With this restriction, we may add the point ion energy of interaction to the indirect interactions obtained from Expression (2.87) to obtain the effective pairwise interactions between the ions. If we denote the total effective pairwise interaction between an ion of type i and an ion of type j separated by a distance $\underline{R}$ by $V_{ij}(|\underline{R}|)$, then we may write

$$V_{AA}(|\underline{R}|) = \frac{2(Z_A)^2}{|\underline{R}|} + \frac{2}{N}\Sigma'_{\{\underline{q}\}} e^{i\underline{q}\cdot\underline{R}}\Big[E_{11}(\underline{q}) - (1-\langle\sigma\rangle_{\underline{R}})(E_{12}(\underline{q})+E_{21}(\underline{q})) + (1-\langle\sigma\rangle_{\underline{R}})^2 E_{22}(\underline{q})\Big] \tag{2.89}$$

$$V_{BB}(|\underline{R}|) = \frac{2(Z_B)^2}{|\underline{R}|} + \frac{2}{N}\Sigma'_{\{\underline{q}\}} e^{i\underline{q}\cdot\underline{R}}\Big[E_{11}(\underline{q}) - (1+\langle\sigma\rangle_{\underline{R}})(E_{12}(\underline{q})-E_{21}(\underline{q})) + (1+\langle\sigma\rangle_{\underline{R}})^2 E_{22}(\underline{q})\Big] \tag{2.90}$$

and

$$V_{AB}(|\underline{R}|) = -\frac{2Z_AZ_B}{|\underline{R}|} + \frac{2}{N}\Sigma'_{\{\underline{q}\}} e^{i\underline{q}\cdot\underline{R}}\Big[E_{11}(\underline{q}) + E_{12}(\underline{q}) - E_{21}(\underline{q}) - \langle\sigma\rangle_{\underline{R}}(E_{12}(\underline{q})+E_{21}(\underline{q})) - (1-\langle\sigma\rangle_{\underline{R}}^2)E_{22}(\underline{q})\Big]. \tag{2.91}$$

By a procedure directly analogous to that followed for a single-element crystal, we have derived expressions for the electronic

contribution to the ordering energy of a binary alloy and for the effective pairwise interactions between the ions in the alloy. The separation of the ordering energy into terms dependent upon the average and the difference pseudopotentials, as in Expression (2.86), was possible only because we expressed the total electronic energy using second order perturbation theory. In addition, the derivation of the effective pairwise interactions necessitated our restricting $f_c(\underline{r})$ to being invariant during changes in the configuration of ions in the crystal at constant volume.

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Chapter Three

EVALUATION OF THE ORDER-DEPENDENT PART OF THE PSEUDOPOTENTIAL

In Chapter Two, we derived an expression for the matrix elements between plane waves of the screened pseudopotential of a metallic binary alloy. We approximated that part of the pseudopotential which arises through the screening of the ionic charges by the conduction electrons with a self-consistent expression which is linear in the unscreened pseudopotential. This approximation was partially motivated by the necessity of avoiding an infinite set of equations which would have had to be solved to obtain the matrix elements of the screening potential. In addition, the approximation was necessary if we were to separate the matrix elements of the screened pseudopotential into the product of a structure-dependent factor and a factor dependent upon the structure for a given volume only through $f_c(\underline{r})$. Apart from this possible dependence through $f_c(\underline{r})$, the entire dependence of the resulting matrix elements of the screened pseudopotential on the positions of the ions during rearrangements of the ions at constant volume is manifest in the two factors, $\delta_{q,\{\underline{K}\}}$ and $F(\underline{q})$. Since $\{\underline{K}\}$ is the set of reciprocal lattice vectors corresponding to the set of ionic sites in the crystal, the Kronecker delta contains only information regarding the points in the crystal which are occupied by ions. If we restrict the final form which we may choose for $f_c(\underline{r})$ to be independent of the configuration of the ions for a given ionic volume, $F(\underline{q})$ contains all the information in the screened

pseudopotential regarding the distribution of the two types of ions on these sites.

We used our expression for the screened pseudopotential to derive perturbation theory expressions for the energy of an individual electronic state, the total conduction electron energy, and the conduction electron contribution to the ordering energy of the alloy. We also derived an expression for the effective pairwise interactions between the ions in the alloy. Since our derivation was directed toward obtaining effective interactions which were invariant during rearrangements of the ions in the crystal at constant volume, we do not need to evaluate a function of $F(\underline{q})$ in order to calculate the effective pairwise interactions. On the other hand, we may wish to calculate a quantity which does depend upon the state of order in the crystal, such as one of the energies which we mentioned above. In this situation, we must evaluate certain functions involving $F(\underline{q})$. We will examine in this chapter the forms in which $F(\underline{q})$ might appear and the information about the crystal which is required to evaluate the order dependence in these cases.

Electron Energies to Second Order in Perturbation Theory

Let us consider a point $\underline{k}$ in reciprocal space such that the wavefunctions of the pseudo-Hamiltonian may be approximated well using a first order perturbation expansion in the pseudopotential and the energy of that state using a second order perturbation expansion in

the pseudopotential. By this we mean that the contributions of higher order terms in the pseudopotential are quite small. As we noted in the previous chapter, standard perturbation theory yields the following expressions for the wavefunction $\bar{v}$ and the energy E_v:

$$|\bar{v}\rangle_{\underline{k}} = a_o(\underline{k})\left[|\underline{k}\rangle + \Sigma'_{\{\underline{q}\}} \frac{|\underline{k}+\underline{q}\rangle\langle\underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2}\right] \tag{3.1}$$

$$E_v = |\underline{k}|^2 + \bar{V}_L + \langle\underline{k}|W|\underline{k}\rangle + \Sigma'_{\{\underline{q}\}} \frac{\langle\underline{k}|W|\underline{k}+\underline{q}\rangle\langle\underline{k}+\underline{q}|W|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2}\ , \tag{3.2}$$

where the primed sum over $\{\underline{q}\}$ includes all reciprocal space vectors but $\underline{q} = 0$. The form which we derived previously for the matrix elements of the pseudopotential is

$$\langle\underline{k}+\underline{q}|W|\underline{k}\rangle = \delta_{\underline{q},\{\underline{K}\}}\langle\underline{k}+\underline{q}|\bar{w}|\underline{k}\rangle + F(\underline{q})\langle\underline{k}+\underline{q}|\Delta w|\underline{k}\rangle\ , \tag{3.3}$$

where $F(\underline{q})$ is given by

$$F(\underline{q}) \equiv \Sigma_{\{\underline{R}\}}\ (\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})\ \frac{e^{-i\underline{q}\cdot\underline{R}}}{N}\ . \tag{3.4}$$

If we substitute Equation (3.3) into Equations (3.1) and (3.2), and note that $\delta_{\underline{q},\{\underline{K}\}}\ F(\underline{q})$ is identically zero, we may express the wavefunction as

$$|\bar{v}\rangle_{\underline{k}} = a_o(\underline{k})\left\{|\underline{k}\rangle + \Sigma'_{\{\underline{K}\}} \frac{|\underline{k}+\underline{K}\rangle\langle\underline{k}+\underline{K}|\bar{w}|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{K}|^2} + \Sigma_{\{\underline{q}\}} \frac{|\underline{k}+\underline{q}\rangle\langle\underline{k}+\underline{q}|\Delta w|\underline{k}\rangle\ F(\underline{q})}{|\underline{k}|^2-\ |\underline{k}+\underline{q}|^2}\right\}\ , \tag{3.5}$$

and the energy as

$$E_V = |\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|\bar{w}|\underline{k}\rangle$$

$$+ \Sigma'_{\{\underline{K}\}} \frac{\langle \underline{k}|\bar{w}|\underline{k}+\underline{K}\rangle\langle \underline{k}+\underline{K}|\bar{w}|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{K}|^2}$$

$$+ \Sigma_{\{\underline{q}\}} |F(\underline{q})|^2 \frac{\langle \underline{k}|\Delta w|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|\Delta w|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \quad . \tag{3.6}$$

Now $F(\underline{q})$ is just the Fourier transform of the deviation of $\sigma(\underline{R})$ from its average value. Since $F(\underline{q}+\underline{K}) = F(\underline{q})$ for all $\underline{K}$ belonging to $\{\underline{K}\}$, there are just N distinct arguments of $F(\underline{q})$, where N is the total number of ions in the crystal. There is a one-to-one correspondence between these values of $F(\underline{q})$ and the N distinct parameters in $\sigma(\underline{R})$. Since Equation (3.5) depends on $F(\underline{q})$ alone, the wavefunction clearly depends in a detailed way upon the precise configuration of ions in the crystal, as one would expect in the exact wavefunction.

In comparison, the energy of the state depends upon $F(\underline{q})$ only through the product, $|F(\underline{q})|^2 = F(\underline{q})F(-\underline{q})$. If we expand this product using the definition of $F(\underline{q})$, we find that

$$F(\underline{q})F(-\underline{q}) = \Sigma_{\{\underline{R}\}} \Sigma_{\{\underline{R}'\}} (\sigma(\underline{R}) - \langle\sigma\rangle_{\underline{R}})$$

$$\times (\sigma(\underline{R}') - \langle\sigma\rangle_{\underline{R}}) \frac{e^{-i\underline{q}\cdot\underline{R}}}{N} \frac{e^{+i\underline{q}\cdot\underline{R}'}}{N} \quad . \tag{3.7}$$

In this expression, the sums over the sets $\{\underline{R}\}$ and $\{\underline{R}'\}$ are described from the same origin. Let us replace the sum over $\underline{R}'$ with a sum over $\underline{R}''$, where $\underline{R}' = \underline{R} + \underline{R}''$. As before, we note that the crystal may become

arbitrarily large at our discretion and neglect the boundary effects arising from such a translation of origin. The sum over $\{\underline{R}\}$ in Equation (3.7) is now independent of $\underline{q}$. Accordingly, let us define a new average by

$$\langle\sigma(0)\sigma(\underline{R}')\rangle_{\underline{R}} \equiv \Sigma_{\{\underline{R}''\}} \frac{(\sigma(\underline{R}'') - \langle\sigma\rangle_{\underline{R}})(\sigma(\underline{R}''+\underline{R}') - \langle\sigma\rangle_{\underline{R}})}{N} \quad . \tag{3.8}$$

This average allows us to write $|F(\underline{q})|^2$ as

$$|F(\underline{q})|^2 = \Sigma_{\{\underline{R}'\}}\langle\sigma(0)\sigma(\underline{R}')\rangle_{\underline{R}} \frac{e^{i\underline{q}\cdot\underline{R}'}}{N} \quad : \tag{3.9}$$

This same result can be shown to follow directly from the convolution theorem [1]. Since the function $\sigma(\underline{R})$ has been defined such that it has a value of +1 if $\underline{R}$ contains an A ion and a value of -1 if $\underline{R}$ contains a B ion, Equation (3.8) defines a two-particle correlation function. Thus, while perturbation theory as outlined above yields a wavefunction which depends in detail upon the arrangement of ions in the crystal, it yields an electron energy which may be expressed to second order in the pseudopotential simply in terms of a two-particle correlation function.

In conjunction with our discussion of the screening contribution in the previous chapter, and later in conjunction with our discussion of the total conduction electron energy, we noted that the sum of an Expression like (3.1) or (3.2) over all the values of $\{\underline{k}\}$ within the Fermi sphere is often well-defined despite the divergence of certain terms in the sum. We noted also that the sum could have such a magnitude that perturbation theory to some order suffices to describe the

value of the sum despite its inability to approximate well the values of many of the terms. Therefore, we may be able to express the total energy of all the electronic states in the Fermi volume accurately using second-order perturbation theory in the pseudopotential even though we are unable to express the energy of each individual electron in this manner. Accordingly, Expression (3.6) may allow an accurate determination of the total conduction electron energy in many cases. It would follow in these cases that the complete effect of the state of order upon the total conduction electron energy is expressed through only a two-particle correlation function. In addition, the abilities to approximate well the screening potential to first order in the pseudopotential and the total conduction electron energy to second order in the pseudopotential are so closely related that the accuracy of one approximation is most likely similar to the accuracy of the other. As we have emphasized in Chapter Two, the ability to approximate the screening potential to first order in the pseudopotential is central to the results of this work. We must therefore conclude that Expression (3.6) will most likely allow an accurate determination of the total conduction electron energy in those systems which are amenable to the treatment described in this work. There may, of course, be exceptions to this statement. The accuracy of using the perturbation theory procedure described above must be investigated carefully for each particular system.

Electron Energies Arising from a Matrix Diagonalization

If the pseudopotential of an alloy may be separated in the manner of Equation (3.3), we have demonstrated that the order dependence of the total conduction electron energy may most likely be expressed using a two-particle correlation function. However, there may be certain exceptional cases in which we can express the screening potential accurately using first-order perturbation theory, leading to a separation of the pseudopotential, and yet cannot approximate well the total conduction electron energy using second-order perturbation theory. In these cases, we would wish to diagonalize a limited secular matrix to obtain accurate energies for certain conduction electron states in the vicinity of band gaps. These energies would then be used to find the total conduction electron energy. We might also wish to know with accuracy the eigenvalues of electron states in the region of a band gap in some system where perturbation theory may or may not approximate the total conduction electron energy. In either case, we would diagonalize some limited secular matrix. Accordingly, let us consider now the solution of a general secular equation to obtain the eigenvalues. We will express the matrix elements of H_p using a basis set of plane waves which we will label with the indices a, b, c,... . We have already evaluated the matrix elements of the screening potential which occur in the secular equation using first-order perturbation theory. The conduction electron eigenvalues of H_p must then satisfy a determinantal

equation which we may indicate by

$$\begin{bmatrix} (H_p)_{aa} - E & (H_p)_{ab} & (H_p)_{ac} & \cdots \\ (H_p)_{ba} & (H_p)_{bb} - E & (H_p)_{bc} & \cdots \\ (H_p)_{ca} & (H_p)_{cb} & (H_p)_{cc} - E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} = 0 \quad . \tag{3.10}$$

If we multiply out the elements of this determinant, we see that the coefficient of some power of E in the resulting equation has a general form given by

$$(H_p)_{ab}(H_p)_{bc} \cdots (H_p)_{da} \quad . \tag{3.11}$$

We may always arrange the subscripts in such a product so that they form what might be called a circular array, such as ac-cb-be-ed-da. In other words, each plane wave which appears on the left-hand side of one matrix element in a product of matrix elements must also appear somewhere in the product on the right-hand side of a matrix element. If all of the matrix elements involved in a given product are between plane waves such that the difference between the wave vectors is not a member of the set $\{\underline{K}\}$, then the matrix elements of T vanish and $F(\underline{q})$ would appear only in products of the following form: $F(\underline{q}_i)F(\underline{q}_j) \cdots F(\underline{q}_n)$, where $\underline{q}_i + \underline{q}_j + \cdots + \underline{q}_n = 0$. If there were one matrix element in the product such that the difference between the wave vectors were a member of $\{\underline{K}\}$, then the products of $F(\underline{q})$'s would have the same form as above where $\underline{q}_i + \underline{q}_j + \cdots + \underline{q}_n = \{\underline{K}\}$. One can generalize from this to state that the equation for the eigenvalues

of H_p will depend upon $F(\underline{q})$ only through products like

$$F(\underline{q}_i)F(\underline{q}_j) \cdots F(\underline{q}_n) \ , \tag{3.12}$$

where $\underline{q}_i + \underline{q}_j + \cdots + \underline{q}_n$ is a member of the set $\{\underline{K}\}$. We may use the definition of $F(\underline{q})$ to write

$$F(\underline{q}_i)F(\underline{q}_j) \cdots F(\underline{q}_n)$$

$$= \Sigma_{\{\underline{R}_i\}}\Sigma_{\{\underline{R}_j\}}\cdots\Sigma_{\{\underline{R}_n\}}(\sigma(\underline{R}_i)-\langle\sigma\rangle_{\underline{R}}) \frac{e^{-i\underline{q}_i\cdot\underline{R}_i}}{N} (\sigma(\underline{R}_j)-\langle\sigma\rangle_{\underline{R}}) \frac{e^{-i\underline{q}_j\cdot\underline{R}_j}}{N}$$

$$\cdots (\sigma(\underline{R}_n)-\langle\sigma\rangle_{\underline{R}}) \frac{e^{-i\underline{q}_n\cdot\underline{R}_n}}{N} \ . \tag{3.13}$$

Proceeding as before, we may substitute for the parameters involved in the sum as follows: $\underline{R}_j = \underline{R}_i + \underline{R}'_j$; $\underline{R}_k = \underline{R}_i + \underline{R}'_k$; $\cdots$ $\underline{R}_n = \underline{R}_i + \underline{R}'_n$. We will neglect the boundary effects associated with the change in the origins in these sums. The coefficient of $\underline{R}_i$ which occurs in the exponential factor in this new sum is just $\underline{q}_i + \underline{q}_j + \cdots + \underline{q}_n$, which has been demonstrated above to be a member of $\{\underline{K}\}$. Since $\exp(-i\underline{K}\cdot\underline{R}) = 1$ for all members of $\{\underline{R}\}$, we see that the sum over $\{\underline{R}_i\}$ is independent of any value of $\underline{q}$. Accordingly, the product of $F(\underline{q})$'s may be expressed as

$$F(\underline{q}_i)F(\underline{q}_j) \cdots F(\underline{q}_n)$$

$$= \Sigma_{\{\underline{R}'_j\}}\Sigma_{\{\underline{R}'_k\}}\cdots\Sigma_{\{\underline{R}'_n\}}\langle\sigma(0)\sigma(\underline{R}'_j) \cdots \sigma(\underline{R}'_n)\rangle_R \frac{e^{-i\underline{q}_j\cdot\underline{R}'_j}}{N} \cdots \frac{e^{-i\underline{q}_n\cdot\underline{R}'_n}}{N} \ , \tag{3.14}$$

where we have defined a new average by

$$\langle\sigma(0)\sigma(\underline{R}'_j)\cdots\sigma(\underline{R}'_n)\rangle_{\underline{R}}$$

$$\equiv \Sigma_{\{\underline{R}_i\}} \frac{(\sigma(\underline{R}_i)-\langle\sigma\rangle_{\underline{R}})(\sigma(\underline{R}_i+\underline{R}'_j)-\langle\sigma\rangle_{\underline{R}})\cdots(\sigma(\underline{R}_i+\underline{R}'_n)-\langle\sigma\rangle_{\underline{R}})}{N} . \qquad (3.15)$$

If we start with a general product of $F(\underline{q})$'s, we may, in many instances, separate this product into two or more smaller products such that the sum of the arguments in each of the smaller products is a member of $\{\underline{K}\}$. When we have separated the product in this manner into the smallest possible sub-products and we find that the sub-products have $M_1, M_2, \ldots, M_m$ factors of $F(\underline{q})$ in each, respectively, then the above discussion demonstrates that the large product depends upon M_1-, M_2-,...,M_m-particle correlation functions. A diagonalization of the full secular matrix would involve a basis consisting of all plane waves of the set $\{\underline{k}\}$. Accordingly, we might expect that we will have one product of $F(\underline{q})$'s in the equation for the energy eigenvalues which will depend upon an N-particle correlation function. Therefore, the energy eigenvalues will depend upon 2-, 3-,..., N-particle correlation functions as we would expect for an exact solution.

With this general result in mind, let us be more specific in our consideration of the form in which $F(\underline{q})$ might be expected to occur in a final expression. We have examined two extreme situations. If we may use perturbation theory to express the quantity which we require, whether it be the energy of an individual electron or the total conduction electron energy, then we have seen that the wavefunction depends upon the detailed arrangement of the ions in the crystal, while

the energies depend upon this arrangement only through a two-particle correlation function. In the other extreme of having to diagonalize a full secular matrix, we found that both the energies and the wavefunctions depend in detail upon the arrangement of ions in the crystal. We will turn now to the cases where we may use a perturbation expansion in the pseudopotential coupled with a limited diagonalization to obtain the eigenvalues.

Electron Energies Arising from a Selective Mixture of Perturbation Theory and Matrix Diagonalization

In the totally disordered crystal, the conduction electrons see no regular arrangement of ions as they travel throughout the crystal. These electrons might be reasonably expected to react essentially as though they were in a lattice of the "average" ions. Therefore, one would expect to find band gaps at values of $\underline{k}$ such that $|\underline{k}|^2 = |\underline{k}+\underline{K}|^2$, where $\underline{K}$ is any member of the set $\{\underline{K}\}$. In a completely ordered crystal, the periodic array is described by a subset of $\{\underline{R}\}$ which we have denoted by $\{\underline{R}_s\}$. We can now construct a set of reciprocal vectors in analogy to the set $\{\underline{K}\}$ such that, for each member of the set, $\underline{K}_s$, $\exp(-i\underline{K}_s\cdot\underline{R}_s) = 1$ for all members of $\{\underline{R}_s\}$. The set $\{\underline{K}_s\}$, which contains all the vectors satisfying the above condition, contains $\{\underline{K}\}$ as a subset. Now we rigorously expect band gaps to occur at all points $\underline{k}$ such that $|\underline{k}|^2 = |\underline{k}+\underline{K}_s|^2$, where $\underline{K}_s$ may be any member of $\{\underline{K}_s\}$. As the temperature of the crystal increases, we would then expect that

the band gaps associated with those members of $\{\underline{K}_s\}$ not included in $\{\underline{K}\}$ would gradually disappear, in correspondence to the disappearance of long-range order in the crystal. We would not expect band gaps to occur at values of $\underline{k}$ which are not suggested by the set $\{\underline{K}_s\}$. We should then like to conclude that we could always treat the matrix elements of the pseudopotential between plane waves whose wave vectors differ by $\underline{q}$ as a perturbation for temperatures outside the critical region, providing that $\underline{q}$ is not a member of $\{\underline{K}_s\}$.

We have mathematical support for such a conclusion. We may rewrite Equation (3.6) to remove explicitly the sum over $\{\underline{K}_s\}$ from the sum over $\{\underline{q}\}$. We may then express E_v by

$$E_v = |\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|\bar{w}|\underline{k}\rangle + \Sigma_{\{\underline{K}\}} \frac{\langle \underline{k}|\bar{w}|\underline{k}+\underline{K}\rangle\langle \underline{k}+\underline{K}|\bar{w}|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{K}|^2}$$

$$+ \Sigma_{\{\underline{K}_s\}} |F(\underline{K}_s)|^2 \frac{\langle \underline{k}|\Delta w|\underline{k}+\underline{K}_s\rangle\langle \underline{k}+\underline{K}_s|\Delta w|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{K}_s|^2}$$

$$+ \sum_{\{\underline{q}\}\neq\{\underline{K}_s\}} |F(\underline{q})|^2 \frac{\langle \underline{k}|\Delta w|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|\Delta w|\underline{k}\rangle}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \quad . \tag{3.16}$$

We should now examine the expected behavior of $|F(\underline{q})|^2$ as a function of temperature. For an alloy which is above its critical region of temperature, $|F(\underline{q})|^2$ is of order N^{-1} for all $\underline{q}$ which are not members of $\{\underline{K}\}$. As the temperature of the alloy decreases, we expect that $|F(\underline{K})|^2$ will increase for those members of $\{\underline{K}_s\}$ which are not members of $\{\underline{K}\}$. In the completely ordered state, $|F(\underline{K}_s)|^2$ is of order N^0 for

all members of $\{\underline{K}_s\}$ which are not members of $\{\underline{K}\}$. Except in the limiting case of a completely ordered crystal, there will always be at least a small range of values of $\underline{q}$ about each member of $\{\underline{K}_s\}$ which is not a member of $\{\underline{K}\}$ such that $|F(\underline{q})|^2$ is similar in magnitude to $|F(\underline{K}_s)|^2$. Returning to Equation (3.16), we shall examine the behavior of the sums in that equation for the case of an alloy below its critical region of temperature. In the completely ordered alloy, $|F(\underline{q})|^2$ is of order N^{-1} for all $\underline{q}$ which are not members of $\{\underline{K}_s\}$. The number of values of $\underline{q}$ included in the last sum in Equation (3.16) is of order N^{+1}. Therefore, this sum approaches an integral as N becomes arbitrarily large, while the nature of the other sums does not change. The type of singularity caused by the denominators in Equation (3.16) gives rise to a singularity in a sum but may be treated when it occurs in an integral by taking the principal part. This was discussed in connection with the derivations of both the screening potential and the total conduction electron energy. Accordingly, a singularity in one of the first two sums in Equation (3.16) is undefined for the ordered crystal and signifies a breakdown of perturbation theory leading to a band gap. However, the principal part of the integral represented by the last sum in Equation (3.16) is well defined and we have no reason to expect a breakdown in the perturbation formalism or a band gap. As we increase the temperature of the alloy, $|F(\underline{K}_s)|^2$ will begin to decrease and we will find a slight range of $\underline{q}$ values about each $\underline{K}_s$ such that

$|F(\underline{q})|^2$ is similar in magnitude to $|F(\underline{K}_s)|^2$. As the alloy approaches the critical temperature, it will eventually reach a temperature at which we may no longer treat those matrix elements for $\underline{q}$ similar to a member of $\{\underline{K}_s\}$ using perturbation theory. At this point, our procedure for avoiding the problem of solving a large secular matrix breaks down. We will discuss this region about the critical temperature in greater detail at the end of this section. For those temperatures below this region about the critical temperature, we shall use perturbation theory to treat all those matrix elements involving $F(\underline{q})$ where $\underline{q}$ is not a member of $\{\underline{K}_s\}$. If the alloy is above this region, we have noted that $|F(q)|^2$ is of order N^{-1} for all values of q which are not members of $\{\underline{K}\}$. Accordingly, for an alloy above this region about the critical temperature, we shall treat all those matrix elements involving $F(\underline{q})$ for $\underline{q}$ not a member of $\{\underline{K}\}$ using perturbation theory. An alloy at a temperature in the immediate vicinity of the critical temperature may not be treated in this manner.

On the basis of this discussion, let us consider the problem of finding the eigenvalue of H_p in the state $\bar{v}$ using the formalism described by Pratt and Zeiger [2]. We can expand $\bar{v}$ in a basis of the set of plane waves $\{\underline{k}\}$. We shall denote by $\{\underline{q}''\}$ that set of plane waves, $\underline{k}+\underline{q}''$, whose interaction with $\bar{v}$ may be treated by perturbation theory. The set $\{\underline{q}''\}$ includes those plane waves which we discussed above as being amenable to a perturbation treatment plus those other plane waves which are sufficiently removed in energy from the state $\bar{v}$

to allow a perturbation treatment of their interaction with $\bar{v}$. All other plane waves in $\{\underline{k}\}$ are placed in the set $\{\underline{q}'\}$. Accordingly, we may write $\bar{v}$ as

$$|\bar{v}\rangle = \Sigma_{\{\underline{q}'\}}\, a_{\underline{q}'}(\underline{k})|\underline{k}+\underline{q}'\rangle + \Sigma_{\{\underline{q}''\}}\, a_{\underline{q}''}(\underline{k})|\underline{k}+\underline{q}''\rangle \ . \tag{3.17}$$

If we operate on this expression for $\bar{v}$ with $-W = T - H_p$ and recall that the eigenvalue of T in the state $\underline{k}+\underline{q}$ is $(|\underline{k}+\underline{q}|^2 + \bar{V}_L)$, we obtain

$$-W|\bar{v}\rangle = \Sigma_{\{\underline{q}'\}}(|\underline{k}+\underline{q}'|^2 + \bar{V}_L - E_v)\, a_{\underline{q}'}(\underline{k})|\underline{k}+\underline{q}'\rangle$$
$$+ \Sigma_{\{\underline{q}''\}}(|\underline{k}+\underline{q}''|^2 + \bar{V}_L - E_v)\, a_{\underline{q}''}(\underline{k})|\underline{k}+\underline{q}''\rangle \ . \tag{3.18}$$

Now let us operate on Equation (3.18) from the left with a plane wave $\underline{k}+\underline{Q}''$ of the set $\{\underline{q}''\}$, obtaining

$$-\langle\underline{k}+\underline{Q}''|W|\bar{v}\rangle = (|\underline{k}+\underline{Q}''|^2 + \bar{V}_L - E_v)\, a_{\underline{Q}''}(\underline{k}) \ . \tag{3.19}$$

We have assumed that perturbation theory suffices to describe the interaction between $\bar{v}$ and the members of the set $\{\underline{q}''\}$. Therefore, we may divide by the energy difference in Equation (3.19), and have confidence that the net contribution of all the members of $\{\underline{q}''\}$ will be well approximated even though this particular energy difference may vanish. If we expand $\bar{v}$ according to Equation (3.17), we may write Equation (3.19) as

$$a_{\underline{Q}''}(\underline{k}) = \Sigma_{\{\underline{q}'\}} \frac{\langle\underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}'\rangle\, a_{\underline{q}'}(\underline{k})}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L} + \Sigma_{\{\underline{q}''\}} \frac{\langle\underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}''\rangle\, a_{\underline{q}''}(\underline{k})}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L} \ . \tag{3.20}$$

We may now substitute for $a_{q''}(\underline{k})$ on the right-hand side of Equation (3.20) using the value established for the left-hand side. Iterating this procedure, we obtain

$$a_{\underline{Q}''}(\underline{k}) = \Sigma_{\{\underline{q}'\}} \frac{\langle \underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}'\rangle\, a_{\underline{q}'}(\underline{k})}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L}$$

$$+ \Sigma_{\{\underline{q}'\}}\Sigma_{\{\underline{q}''\}} \frac{\langle \underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}''\rangle}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L} \frac{\langle \underline{k}+\underline{q}''|W|\underline{k}+\underline{q}'\rangle a_{\underline{q}'}(\underline{k})}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} + \cdots \qquad (3.21)$$

Keeping terms only to second-order in the pseudopotential, we can extract the sum over $\{\underline{q}'\}$ from the series to write

$$a_{\underline{Q}''}(\underline{k}) = \Sigma_{\{\underline{q}'\}}\, a_{\underline{q}'}(\underline{k}) \left\{ \frac{\langle \underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}'\rangle}{E_v - |\underline{k}+\underline{Q}''| - \bar{V}_L} \right.$$

$$\left. + \Sigma_{\{\underline{q}''\}} \frac{\langle \underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}''\rangle}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L} \frac{\langle \underline{k}+\underline{q}''|W|\underline{k}+\underline{q}'\rangle}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} \right\} . \qquad (3.22)$$

We can use Equation (3.22) to write $\bar{v}$ to second-order in the pseudopotential. Expression (3.17) becomes

$$|\bar{v}\rangle = \Sigma_{\{\underline{q}'\}}\, a_{\underline{q}'}(\underline{k}) \left\{ |\underline{k}+\underline{q}'\rangle + \Sigma_{\{\underline{q}''\}} |\underline{k}+\underline{q}''\rangle \frac{\langle \underline{k}+\underline{q}''|W|\underline{k}+\underline{q}'\rangle}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} \right.$$

$$\left. + \Sigma_{\{\underline{q}''\}}\Sigma_{\{\underline{Q}''\}} |\underline{k}+\underline{q}''\rangle \frac{\langle \underline{k}+\underline{q}''|W|\underline{k}+\underline{Q}''\rangle}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} \frac{\langle \underline{k}+\underline{Q}''|W|\underline{k}+\underline{q}'\rangle}{E_v - |\underline{k}+\underline{Q}''|^2 - \bar{V}_L} \right\} . \qquad (3.23)$$

If we operate on Equation (3.18) from the left with a plane wave $\underline{k}+\underline{Q}'$ of the set $\{\underline{q}'\}$, we obtain an equation analogous to Equation (3.19),

$$-\langle \underline{k}+\underline{Q}'|W|\bar{v}\rangle = (|\underline{k}+\underline{Q}'|^2 + \bar{V}_L - E_v)\, a_{\underline{q}'}(\underline{k}) \quad . \tag{3.24}$$

We may substitute for $\bar{v}$ using Equation (3.23) to obtain the following secular equation from Equation (3.24):

$$\Sigma_{\{q'\}}(\langle \underline{k}+\underline{Q}'|H_{eff}|\underline{k}+\underline{q}'\rangle - E_v\, \delta_{\underline{q}',\underline{Q}'}) = 0 \quad , \tag{3.25}$$

where the matrix elements of H_{eff} are given to second-order in the pseudopotential by

$$\langle \underline{k}+\underline{Q}'|H_{eff}|\underline{k}+\underline{q}'\rangle = (|\underline{k}+\underline{Q}'|^2 + \bar{V}_L)\delta_{\underline{q}',\underline{Q}'} + \langle \underline{k}+\underline{Q}'|W|\underline{k}+\underline{q}'\rangle$$
$$+ \Sigma_{\{\underline{q}''\}} \frac{\langle \underline{k}+\underline{Q}'|W|\underline{k}+\underline{q}''\rangle\langle \underline{k}+\underline{q}''|W|\underline{k}+\underline{q}'\rangle}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} \quad . \tag{3.26}$$

We should note that this secular equation involves only matrix elements of H_{eff} between plane waves of the type $\underline{k}+\underline{q}'$ where $\underline{q}'$ is a member of the set $\{\underline{q}'\}$. We have expressed the interaction between the state $\bar{v}$ and the plane waves of the set $\{\underline{q}''\}$ in terms of perturbation theory. The presence of the final energy, E_v, in the matrix elements of H_{eff} underscores the fact that the secular matrix equation indicated by Equation (3.25) is appropriate only for finding the energy and wavefunction associated with the single state $\bar{v}$. In other words, the diagonalization of the matrix will yield only one actual eigenstate, not several as is usually the case. We also note that the solution of the secular equation would involve an iterative procedure in E_v. For these reasons, the procedure which we have outlined here is not particularly convenient for actual calculations involving the

pseudopotential. On the other hand, the form of the matrix elements of H_{eff} given in Equation (3.26) allows us to make some general statements regarding the form in which $F(\underline{q})$ occurs in expressions for the energy.

If we are considering an alloy at a temperature above the region immediately about the critical temperature, as discussed previously, then we may consider the set $\{\underline{q}''\}$ as consisting of all the vectors of the set $\{\underline{k}\}$ which are not of the form $\underline{k}+\underline{K}$, where $\underline{K}$ is a member of the set $\{\underline{K}\}$. In addition, most of the vectors in the set $\{\underline{K}\}$ may also be included in $\{\underline{q}''\}$. The set $\{\underline{q}'\}$ contains only certain members of the set $\{\underline{K}\}$. Therefore, we would expect that all of the matrix elements of H_{eff} would have a form indicated by

$$\langle \underline{k}+\underline{K}|H_{eff}|\underline{k}+\underline{K}'\rangle = (|\underline{k}+\underline{K}|^2+\bar{V}_L)\delta_{\underline{K},\underline{K}'} + \langle \underline{k}+\underline{K}|\bar{w}|\underline{k}+\underline{K}'\rangle$$

$$+ \Sigma_{\{\underline{K}''\}} \frac{\langle \underline{k}+\underline{K}|\bar{w}|\underline{k}+\underline{K}''\rangle\langle \underline{k}+\underline{K}''|\bar{w}|\underline{k}+\underline{K}'\rangle}{E_v - |\underline{k}+\underline{K}''|^2 - \bar{V}_L}$$

$$+ \Sigma_{\{\underline{q}''\}} \frac{\langle \underline{k}+\underline{K}|\Delta w|\underline{k}+\underline{q}''\rangle\langle \underline{k}+\underline{q}''|\Delta w|\underline{k}+\underline{K}'\rangle|F(\underline{q})|^2}{E_v - |\underline{k}+\underline{q}''|^2 - \bar{V}_L} , \quad (3.27)$$

where the sums include only members of $\{\underline{q}''\}$. For the case of an alloy above its critical temperature, Equation (3.27) demonstrates that $F(\underline{q})$ appears in the secular equation only in the form $|F(\underline{q})|^2$, which may be evaluated in terms of two-particle correlations. Therefore, the individual eigenfunctions and eigenvalues of H_p have been shown to depend upon the arrangements of ions in the alloy crystal only through a two-

particle correlation function if the alloy is above its critical temperature. This result depends upon our ability to treat the interaction between a given state $\underline{k}$ and all those states $\underline{k}+\underline{q}$, for $\underline{q}$ not a member of $\{\underline{K}\}$, using perturbation theory.

If we are considering an alloy at a temperature below the region immediately about its critical temperature, the set $\{q''\}$ contains all members of the set $\{\underline{k}\}$ except for certain members of $\{\underline{K}_s\}$. Therefore, the set $\{\underline{q}'\}$ will contain only certain members of $\{\underline{K}_s\}$. We would expect that the secular Equation (3.25) would contain three types of matrix elements of H_{eff}. One of these types is just Expression (3.27). If we let $\underline{K}_a$, $\underline{K}_b$, and $\underline{K}_c$ be members of $\{\underline{K}_s\}$ but not members of $\{\underline{K}\}$, then we may write the other two types of matrix elements as

$$\langle \underline{k}+\underline{K}_a|H_{eff}|\underline{k}+\underline{K}\rangle = \langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}\rangle\ F(\underline{K}_a)$$

$$+ \Sigma_{\{\underline{K}''\}} \frac{\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}''\rangle\langle \underline{k}+\underline{K}''|\bar{w}|\underline{k}+\underline{K}\rangle\ F(\underline{K}_a)}{E_v-|\underline{k}+\underline{K}''|^2-\bar{V}_L}$$

$$+ \Sigma_{\{\underline{K}''_c\}}(\delta_{\underline{K}_a-\underline{K}''_c,\{\underline{K}\}}\langle \underline{k}+\underline{K}_a|\bar{w}|\underline{k}+\underline{K}''_c\rangle + F(\underline{K}_a-\underline{K}''_c)\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}''_c\rangle$$

$$\times \frac{\langle \underline{k}+\underline{K}''_c|\Delta w|\underline{k}+\underline{K}\rangle\ F(\underline{K}''_c)}{E_v-|\underline{k}+\underline{K}''_c|^2-\bar{V}_L}$$

$$+ \sum_{\{\underline{q}''\}\neq\{\underline{K}''_c\}} \frac{\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{q}''\rangle\langle \underline{k}+\underline{q}''|\Delta w|\underline{k}+\underline{K}\rangle\ F(\underline{q}'')F(\underline{K}_a-\underline{q}'')}{E_v-|\underline{k}+\underline{q}''|^2-\bar{V}_L}\ , \qquad (3.28)$$

and

$$\langle \underline{k}+\underline{K}_a|H_{eff}|\underline{k}+\underline{K}_b\rangle = (|\underline{k}+\underline{K}_a|^2+\bar{V}_L)\delta_{\underline{K}_a,\underline{K}_b}$$

$$+ (\delta_{\underline{K}_a-\underline{K}_b,\{\underline{K}\}}\langle \underline{k}+\underline{K}_a|\bar{w}|\underline{k}+\underline{K}_b\rangle + F(\underline{K}_a-\underline{K}_b)\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}_b\rangle)$$

$$+ \Sigma_{\{\underline{K}''\}} \frac{\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}''\rangle\langle \underline{k}+\underline{K}''|\Delta w|\underline{k}+\underline{K}_b\rangle\ F(\underline{K}_a)\ F(-\underline{K}_b)}{E_v-|\underline{k}+\underline{K}''|^2-\bar{V}_L}$$

$$+ \Sigma_{\{\underline{K}''_c\}}(\delta_{\underline{K}_a-\underline{K}''_c,\{\underline{K}\}}\langle \underline{k}+\underline{K}_a|\bar{w}|\underline{k}+\underline{K}''_c\rangle + F(\underline{K}_a-\underline{K}''_c)\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{K}''_c\rangle)$$

$$\times \frac{(\delta_{\underline{K}''_c-\underline{K}_b,\{\underline{K}\}}\langle \underline{k}+\underline{K}''_c|\bar{w}|\underline{k}+\underline{K}_b\rangle + F(\underline{K}''_c-\underline{K}_b)\langle \underline{k}+\underline{K}''_c|\Delta w|\underline{k}+\underline{K}_b\rangle)}{E_v-|\underline{k}+\underline{K}''_c|^2-\bar{V}_L}$$

$$+ \Sigma_{\{\underline{q}''\}\neq\{\underline{K}''_c\}} \frac{\langle \underline{k}+\underline{K}_a|\Delta w|\underline{k}+\underline{q}''\rangle\langle \underline{k}+\underline{q}''|\Delta w|\underline{k}+\underline{K}_b\rangle\ F(\underline{K}_a-\underline{q}'')\ F(\underline{q}''-\underline{K}_b)}{E_v-|\underline{k}+\underline{q}''|^2-\bar{V}_L}, \qquad (3.29)$$

where the sums include only members of $\{\underline{q}''\}$. It is clear that at least Equation (3.28) contains factors, like $F(\underline{K}_a)$ and $F(\underline{K}_a-\underline{q})F(\underline{q})$, which cannot satisfy the condition that the sum of the arguments is a member of $\{\underline{K}\}$. Accordingly, not all of the matrix elements of the secular matrix may be evaluated in terms of few-particle correlation functions. Some of the terms depend upon the exact configuration of ions in the crystal, as discussed earlier. Therefore, the electronic eigenfunctions which arise from the solution of the secular equation depend upon the precise configuration of the ions. We know, however, from our previous analysis of a matrix diagonalization, that the products which occur in the equation which we solve for the energy will be such that the sum of the arguments is a member of $\{\underline{K}\}$. Let us proceed to examine the types

of products which will occur when we multiply out a determinant, the elements of which are like Equations (3.27), (3.28), and (3.29). In order to be consistent in our perturbation expansion, we will drop all those terms which involve more than one factor of the ratio of a matrix element of the pseudopotential to an energy difference, such as

$$\frac{\langle \underline{k} + \underline{q}'' | \Delta w | \underline{k} + \underline{K} \rangle}{E_v - |\underline{k} + \underline{q}''| - \bar{V}_L} \quad . \tag{3.30}$$

We must pause to investigate the nature of the set of vectors $\{\underline{K}_a\}$, which is that subset of $\{\underline{K}_s\}$ which is not included in $\{\underline{K}\}$. We are interested in the maximum number of different values of $\underline{K}_a$ which might have to be considered before the sum of them becomes a member of the set $\{\underline{K}\}$. This determines the maximum number of $F(\underline{q})$'s needed to obtain a product such that the sum of the arguments is a member of $\{\underline{K}\}$, and thus the maximum number of particles whose correlations we must know in order to evaluate the electronic eigenvalues as we outlined above. Let us consider a 50-50 alloy which orders in the cesium chloride structure. The set $\{\underline{K}\}$ consists of those reciprocal lattice vectors associated with the body-centered cubic arrangement of ionic sites, while the set $\{\underline{K}_s\}$ consists of those reciprocal lattice vectors associated with the simple cubic lattice points of the ordered system. In this system, the sum of any two members of the set $\{\underline{K}_a\}$, as defined above, is a member of $\{\underline{K}\}$. This is a special property of such a system

which we shall need in our discussion of the products of the matrix elements of $\overline{H}_{eff}$. By way of comparison, let us consider a 25-75 alloy which orders on a lattice of ionic sites having face-centered cubic symmetry. The set $\{\underline{K}\}$ consists of the reciprocal lattice vectors associated with the face-centered cubic array of ionic sites, while the set $\{\underline{K}_s\}$ consists of those reciprocal lattice vectors associated with the simple cubic symmetry of the ordered system. In this case, we may add two vectors of $\{\underline{K}_a\}$ and obtain either a member of $\{\underline{K}\}$ or another member of $\{\underline{K}_a\}$. If we are considering a large product of $F(q)$'s such that the sum of the arguments is a member of $\{\underline{K}\}$, we wish to break the large product up into the smallest sub-products such that the sum of the arguments in each sub-product is also a member of $\{\underline{K}\}$. The number of factors in the largest of these sub-products will tell us the highest number of particles whose correlations we must consider to evaluate the large product. In each of these large products, the nature of $\{\underline{K}_a\}$ for this fcc system is such that we should never need the sum of more than three vectors of $\{\underline{K}_a\}$ to obtain a member of $\{\underline{K}\}$. With these properties in mind, let us return to our consideration of the secular equation.

As we noted in our discussion of an alloy at a temperature above its critical temperature, matrix elements like Expression (3.27) may be evaluated in terms of two-particle correlations. Turning to the other matrix elements, let us consider first the case of a 50-50 alloy which orders in the cesium chloride structure. Since all the members

of $\{\underline{K}_a\}$ in this system are related to one member of $\{\underline{K}_a\}$ by vectors of the set $\{\underline{K}\}$, we never need the sum of more than two members of $\{\underline{K}_a\}$ to obtain a member of the set $\{\underline{K}\}$. Accordingly, all the factors like $F(\underline{K}_a - \underline{K}_c)$ in Equations (3.28) and (3.29) are zero, and $F(\underline{K}_a) = F(\underline{K}''_c)$ for all $\underline{K}''_c$. Thus, Equation (3.29) may be evaluated and depends on the arrangement of ions for a given ionic volume only through the two-particle correlation function dependence of $|F(\underline{K}_a)|^2$ and $|F(\underline{K}_a - \underline{q}'')|^2$. Since we have dropped from the product of matrix elements of H_{eff} all those terms which involve more than one factor like (3.30), Expressions like (3.28) give rise only to products like $|F(\underline{K}_a)|^2$ and $F(\underline{K}_a - \underline{q}'') \times F(\underline{q}'')F(-\underline{K}_a)$. The former product requires a knowledge of two-particle correlations, while the latter requires a limited knowledge of three-particle correlations.

In conclusion, a 50-50 alloy ordering in the cesium chloride structure will possess electronic eigenvalues which require a knowledge of at least two- and three-particle correlations for their evaluation below the critical temperature of the alloy. This result depends upon our perturbation treatment of certain matrix elements as we discussed above.

If we now turn to the consideration of the 25-75 alloy which we described earlier, an analysis similar to the preceding discussion reveals that we must evaluate products of $F(\underline{q})$ like those above. In addition, even if we drop all terms involving more than one factor like Equation (3.30), we must evaluate products like $F(\underline{K}_a)F(\underline{K}_b - \underline{K}_a)F(-\underline{K}_b)$

and $F(\underline{K}_a - \underline{q}'')F(\underline{q}'')F(\underline{K}_b - \underline{K}_a)F(-\underline{K}_b)$. Therefore, it is clear that a 25-75 alloy such as this will possess electrons whose eigenvalues require a knowledge of at least two-, three-, and four-particle correlations for their evaluation below the critical temperature of the alloy. It is apparent that more complicated structures will require a knowledge of the correlations among larger numbers of particles.

We have been discussing the likely form of expressions for the individual electron eigenvalues which arise from treating the electron states using a selective mixture of perturbation theory and matrix diagonalization. As we noted previously, the total conduction electron energy may most likely be evaluated in terms of two-particle correlations in those systems in which the pseudopotential may be placed to a good approximation in the form of Equation (3.3). In these instances, the influence of those correlations among more than two particles which appear in the expressions for some of the eigenvalues of individual electrons must cancel in some way when the eigenvalues of all the conduction electrons are added together to yield the total conduction electron energy. Otherwise, the total conduction electron energy must also depend on these correlations. There is a correspondence between the accuracy of a perturbation expansion of the total conduction electron energy to second-order in the pseudopotential and the cancellation of the effects of these higher order correlations. Of course, perturbation theory results may also be inaccurate due to the nature of the structure-independent part of the pseudopotential. In the region

about the critical temperature which we discussed before, we cannot use perturbation theory to avoid the solution of a large secular matrix since $|F(\underline{q})|^2$ is of order N^0 for a continuous range of values about each member of $\{\underline{K}_s\}$. Therefore, we expect that the eigenvalues of individual electrons will depend in general upon correlations among large numbers of particles. To the extent that the influence of these correlations fails to cancel when we sum over the individual electron energies to obtain the total conduction electron energy, we will find that the total conduction electron energy depends upon N-particle correlations in this region. This corresponds to the appearance of critical scattering phenomena at temperatures in the vicinity of the critical temperature.

In summary, we showed that we may express the total conduction electron energy of the crystal in terms of two-particle correlations if this energy may be approximated well through a second-order perturbation expansion in the pseudopotential given by Equation (3.3). Then we demonstrated that the eigenvalues of individual electrons obtained from the solution of a secular equation of dimension M might be expected to depend upon correlations between as many as M particles. We discussed the approximation that the matrix elements of the pseudopotential between plane waves whose wave vectors differ by some $\underline{q}$ may always be treated in a perturbation expansion, where $\underline{q}$ could be any vector but a member of $\{\underline{K}\}$ in an alloy above the region about the critical temperature, and any vector but a member of $\{\underline{K}_s\}$ in an alloy below this

critical region. Using this approximation, we demonstrated that a solution of a secular equation for an alloy at a temperature above this critical region yields individual electron eigenvalues which depend upon the arrangement of the ions only through a two-particle correlation function. Below this critical region, the electronic eigenvalues depend upon the arrangement of the ions through correlation functions among two, three, and even greater numbers of particles. The total conduction electron energy will also depend upon these correlations unless their influence cancels in some way when the electron eigenvalues are summed over the Fermi volume, as we discussed previously. Apart from this possible cancellation, the total conduction electron energy will therefore depend upon two-particle correlations above the critical region and upon at least two- and three-particle correlations below the critical region. There is also a region about the critical temperature in which both the energies of individual electrons and the total conduction electron energy may depend upon correlations among N-particles. In the absence of information regarding correlations among greater numbers of particles than two, we are accordingly restricted to the evaluation of either those energies for which perturbation theory is completely applicable, or energies in an alloy which is either completely ordered or in the temperature region above the critical region.

The Expression of $|F(\underline{q})|^2$ in Terms of Cowley Order Parameters

We wish to express $|F(\underline{q})|^2$ in terms of well established two-particle correlation parameters. The Cowley order parameters [3], $\alpha(\underline{R})$, are a convenient set to use for this purpose. Let us define $p_A(\underline{R})$ and $p_B(\underline{R})$ as the probabilities of finding an A ion located at the site $\underline{R}$ if the origin contains an A ion or a B ion, respectively. If x is the fraction of ions in the crystal which are of type A, then we may define the Cowley order parameters by

$$\alpha(\underline{R}) \equiv 1 - \frac{p_B(\underline{R})}{x} \quad . \tag{3.31}$$

Since the probability of finding an A ion at the origin simultaneously with a B ion at $\underline{R}$ must always equal the probability of finding a B ion at the origin simultaneously with an A ion at $\underline{R}$, we can establish the following relationship between $p_A(\underline{R})$ and $p_B(\underline{R})$:

$$x(1 - p_A(\underline{R})) = (1 - x)\, p_B(\underline{R}) \quad . \tag{3.32}$$

This relationship allows us to define $\alpha(\underline{R})$ in an equivalent way in terms of $p_A(\underline{R})$ by

$$\alpha(\underline{R}) \equiv \frac{p_A(\underline{R}) - x}{x} \quad . \tag{3.33}$$

We may note two properties of $\alpha(\underline{R})$. First, $\alpha(0)$ is unity. The second property follows from the summation of Equation (3.33) over the complete set of $\{\underline{R}\}$. The sum of $p_A(\underline{R})$ over all values of $\underline{R}$ in $\{\underline{R}\}$ must yield xN, which is just the number of A ions in the crystal. Therefore, $\alpha(\underline{R})$ has the property that

$$\Sigma_{\{\underline{R}\}}\ \alpha(\underline{R}) = \frac{1}{1-x}\,(xN - xN) = 0\ . \tag{3.34}$$

If we turn to the average over the crystal defined in Equation (3.8), we may use the definition of $\langle\sigma\rangle_{\underline{R}}$ in (2.28) to write Equation (3.8) as

$$\langle\sigma(0)\sigma(\underline{R}')\rangle_{\underline{R}} = \Sigma_{\{\underline{R}\}}\ \frac{\sigma(\underline{R})\ \sigma(\underline{R}+\underline{R}')}{N} - \langle\sigma\rangle^2_{\underline{R}}\ . \tag{3.35}$$

But the product of $\sigma(\underline{R})\sigma(\underline{R}+\underline{R}')$ is +1 if both sites $\underline{R}$ and $\underline{R+R'}$ contain the same type of ion and is -1 if the sites contain different types of ions. Accordingly, the average of this product over the set $\{\underline{R}\}$ may be expressed as

$$\begin{aligned}\Sigma_{\{\underline{R}\}}\ \frac{\sigma(\underline{R})\ \sigma(\underline{R}+\underline{R}')}{N} &= x[(+1)\ \ p_A(\underline{R}') + (-1)(1-p_A(\underline{R}'))] \\ &\quad + (1-x)[(+1)(1-p_B(\underline{R}')) + (-1)p_B(\underline{R}')] \\ &= 2x\ p_A(\underline{R}') - 2(1-x)p_B(\underline{R}') + 1 - 2x\ .\end{aligned} \tag{3.36}$$

We may now substitute for $p_A(\underline{R})$ and $p_B(\underline{R})$ from the definitions for $\alpha(\underline{R})$ to obtain

$$\begin{aligned}\Sigma_{\{\underline{R}\}}\ \frac{\sigma(\underline{R})\ \sigma(\underline{R}+\underline{R}')}{N} &= [2x(1-x)]\ \alpha(\underline{R}') + 2x^2 \\ &\quad + [2(1-x)x]\ \alpha(\underline{R}') - 2(1-x)x + 1 - 2x \\ &= [4x(1-x)]\alpha(\underline{R}') + 4x^2 - 4x + 1\ .\end{aligned} \tag{3.37}$$

We may use the definition of $\langle\sigma\rangle_{\underline{R}}$ to write Equation (3.37) as

$$\Sigma_{\{\underline{R}\}}\ \frac{\sigma(\underline{R})\ \sigma(\underline{R}+\underline{R}')}{N} = 4x(1-x)\ \alpha(\underline{R}') + \langle\sigma\rangle^2_{\underline{R}}\ . \tag{3.38}$$

This expression enables us to relate the average in Equation (3.35) to the Cowley order parameters by

$$\langle\sigma(0)\sigma(\underline{R}')\rangle_{\underline{R}} = 4x(1-x)\,\alpha(\underline{R}') \quad . \tag{3.39}$$

Therefore, $|F(\underline{q})|^2$ may be expressed in terms of the Cowley order parameters as

$$|F(\underline{q})|^2 = 4x(1-x)\,\Sigma_{\{\underline{R}\}}\,\frac{\alpha(\underline{R})\,e^{+i\underline{q}\cdot\underline{R}}}{N} \quad . \tag{3.40}$$

The above result may also be obtained through analogy with the expression for the intensity of a diffracted x-ray beam derived by J.M. Cowley [4].

In the case of a completely disordered crystal, $\alpha(\underline{R})$ must be constant for all $\underline{R} \neq 0$. Since $\alpha(0) = 1$ and the sum of $\alpha(\underline{R})$ over all members of $\{\underline{R}\}$ must equal zero, we see that $\alpha(\underline{R})$ must equal $-1/(N-1)$ for $\underline{R} \neq 0$. In this case, $|F(\underline{q})|^2$ is given by

$$|F(\underline{q})|^2 = \frac{4x(1-x)}{N-1}\,(1-\delta_{\underline{q},\{\underline{K}\}}) \quad . \tag{3.41}$$

The case of a completely ordered crystal is not as easily discussed since the exact form of $|F(\underline{q})|^2$ depends upon the particular structure involved. As a simple illustration, let us consider a 50-50 alloy which orders in the cesium chloride structure. The lattice of ionic sites is body-centered cubic. In the ordered state, we may consider that A ions occupy all of the body-centers and B ions occupy all of the corner sites. Accordingly, $\alpha(\underline{R}) = 1$ for all members of $\{\underline{R}\}$ which correspond to the set of repeating vectors for the ordered state,

$\{\underline{R}_s\}$. For all other sites in $\{\underline{R}\}$, $\alpha(\underline{R})$ is equal to $1-(1/x)$, or -1 in this case. Therefore, $|F(q)|^2$ is given by

$$|F(\underline{q})|^2 = 4x(1-x)\left[-\Sigma_{\{\underline{R}\}}\frac{e^{i\underline{q}\cdot\underline{R}}}{N} + \Sigma_{\{\underline{R}_s\}}\frac{e^{i\underline{q}\cdot\underline{R}_s}}{(N/2)}\right] . \tag{3.42}$$

If $\underline{q}$ is any member of the set $\{K\}$, then both sums in Equation (3.42) are unity and $|F(\underline{q})|^2$ vanishes. This is in agreement with the previously discussed property that $F(\underline{K}) = 0$. If $\underline{q}$ is not a member of $\{\underline{K}_s\}$, the set of reciprocal lattice vectors corresponding to $\{\underline{R}_s\}$, then both sums are zero and $|F(\underline{q})|^2$ vanishes. If $\underline{q}$ is a member of $\{\underline{K}_a\}$, which consists of those members of $\{\underline{K}_s\}$ which are not members of $\{\underline{K}\}$, then the first sum is zero and the second is unity. Accordingly, for the ordered case, we may write $|F(\underline{q})|^2$ as

$$|F(\underline{q})|^2 = 4x(1-x)\,\delta_{\underline{q},\{\underline{K}_a\}} . \tag{3.43}$$

One may generalize to state that $|F(\underline{q})|^2$ is zero in the completely ordered state of the alloy except for $\underline{q}$ equal to certain discrete vectors describing the symmetry of the ordered state.

We have expressed $|F(\underline{q})|^2$ in terms of Cowley order parameters as we desired. In addition we have examined the behavior of $|F(\underline{q})|^2$ in the limiting cases of complete order and complete disorder, and found that, for specific structures, we can find simple functional forms for it in both limits. In complete disorder, $|F(\underline{q})|^2$ is a constant except that it vanishes for $\underline{q}$ a member of $\{\underline{K}\}$. In a completely ordered state, $|F(\underline{q})|^2$ is non-vanishing only for certain discrete values of $\underline{q}$.

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Chapter Four

THE SELECTION OF THE PSEUDOPOTENTIAL

In Chapter Two, we discussed the properties of a pseudo-Hamiltonian, H_p, which has the general form suggested by Austin, Heine, and Sham [1],

$$H_p(\underline{r},\underline{r}') = T(\underline{r})\delta(\underline{r}-\underline{r}') + W(\underline{r},\underline{r}') \ , \tag{4.1}$$

where

$$W(\underline{r},\underline{r}') = V^I(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') + \Sigma_c \langle \underline{r}|c\rangle \ f_c(\underline{r}') \ . \tag{4.2}$$

In this expression, $T(\underline{r})$ is the sum of the kinetic energy operator and the potential $\bar{V}_L$. $\bar{V}_L$ is the spatial average over the entire crystal of the Coulomb potential of the nucleii and the Hartree potential of the core and conduction electrons. $V^I(\underline{r},\underline{r}')$ is the Hartree-Fock potential of the ion cores less that part which is included in $\bar{V}_L$. $V^{EL}(\underline{r},\underline{r}')$ is the many-body potential of the conduction electrons less that part which is included in $\bar{V}_L$. In Chapter Two, we approximated this potential with a linearized form of the Hartree potential of the conduction electrons. $\langle \underline{r}|c\rangle$ is the wavefunction of a core state of the actual crystalline Hamiltonian, $H = T + V^I + V^{EL}$. The core state wavefunctions have been assumed to be independent of local environment in the crystal. We shall approximate them with the corresponding atomic wavefunctions in an actual calculation. The sum over "c" in Equation (4.2) extends over all of the core states in the crystal. In the pseudo-Hamiltonian of Austin, Heine, and Sham, $f_c(\underline{r}')$ is an arbitrary function of $\underline{r}'$ and the parameter "c". We found in Chapter Two that the separation of the alloy pseudopotential was possible only when we restricted $f_c(\underline{r}')$ to be independent

of the local environment of the ion with which it is associated, within a particular configuration of ions in the crystal. We emphasized then that this restriction on the final form of $f_c(\underline{r})$ is not an approximation.

In any application of the pseudopotential method, we wish to choose $f_c(\underline{r}')$ in such a way as to obtain the most accurate electronic eigenvalues from the pseudo-Hamiltonian in Equation (4.1). If we could solve the general secular equation exactly, the work of Austin, Heine, and Sham [1] has shown that this pseudo-Hamiltonian would yield the exact electronic eigenvalues. However, as we discussed at length in Chapter Two, the solution of the general secular equation for the alloy problem would involve the solution of a set of at least N linear equations, where N is the number of ions in the crystal. The necessity of avoiding the general solution of such a set of equations and our desire to separate the pseudopotential led us to the necessity of using a linear approximation for the self-consistent screening potential. Linearizing the screening involves using first order perturbation theory to calculate the valence electron eigenfunctions of H_p. Further, as we noted in Chapter Three, the electron energies for a general configuration of ions in the crystal may be calculated using no more than two-particle correlations only if we may represent the total conduction electron energy using second order perturbation theory. Accordingly, we must use perturbation theory in this instance if we have at our disposal no more than two-particle correlation functions. Since our

formalism demands the use of perturbation theory in at least one step in any calculation, we should select that set of functions, $f_c(\underline{r}')$, which optimizes in some way the convergence of a perturbation expansion in the pseudopotential.

Optimization through the Minimization of the Kinetic Energy

Several authors [1,2,3] have decided that this optimization procedure could be accomplished most directly by minimizing the expectation value of the kinetic energy operator in the valence state, denoted by $\bar{v}$, of the pseudo-Hamiltonian, H_p. This minimization condition may be written as

$$\delta\bar{T} = 0 \ , \tag{4.3}$$

where

$$\bar{T} \equiv \frac{\langle\bar{v}|T|\bar{v}\rangle}{\langle\bar{v}|\bar{v}\rangle} \ . \tag{4.4}$$

One of the properties of the pseudo-Hamiltonian of Austin, Heine, and Sham is that the wavefunction of the valence state, $\langle\underline{r}|\bar{v}\rangle$, of H_p differs from that of the valence state, $\langle\underline{r}|v\rangle$, of H by no more than a linear combination of the core state wavefunctions of H [1]. Accordingly, Expression (4.4) may vary only by a change in the coefficients of one or more of the $\langle\underline{r}|c\rangle$ which combine with $\langle\underline{r}|v\rangle$ to yield $\langle\underline{r}|\bar{v}\rangle$. We may vary the coefficient of each $\langle\underline{r}|c\rangle$ separately since there is no constraining relation among these coefficients. Further, we may vary either the bras or the kets in Expression (4.4) independently

since the variation in the coefficient of each core state may be any small complex number. These two variations yield two equations for each core state, both of which must be satisfied by the optimized pseudopotential,

$$\langle c|T|\bar{v}\rangle = \bar{T}\langle c|\bar{v}\rangle \quad , \tag{4.5}$$

and

$$\langle \bar{v}|T|c\rangle = \bar{T}\langle \bar{v}|c\rangle \quad . \tag{4.6}$$

One of these relations may also be deduced from the other through the Hermiticity of T in the set of p ane waves. In order to convert these relations into an equivalent set involving the pseudopotential, we substitute $H_p - W$ for T. If we further note that $H_p|\bar{v}\rangle = E_v|\bar{v}\rangle$ and that $E_v = \bar{T} + \bar{W}$, where

$$\bar{W} \equiv \frac{\langle \bar{v}|W|\bar{v}\rangle}{\langle \bar{v}|\bar{v}\rangle} \quad , \tag{4.7}$$

we may write Equations (4.5) and (4.6) as

$$\langle c|W|\bar{v}\rangle = \bar{W}\langle c|\bar{v}\rangle \tag{4.8}$$

and

$$\langle \bar{v}|W|c\rangle = \bar{W}\langle \bar{v}|c\rangle \quad . \tag{4.9}$$

These two equations, taken together, imply a limited kind of Hermiticity for W. In other words, the matrix elements of W between the state $\bar{v}$ and the set of core states display the Hermitian property. One may now substitute for $\bar{W}$ on the left-hand sides of Equations (4.8) and (4.9) using Equation (4.2). If we rearrange the terms, we can obtain the following two relations:

$$\int d\underline{r}\ f_c(\underline{r})\langle\underline{r}|\bar{v}\rangle = \langle c|(-V^I - V^{EL} + \bar{W})|\bar{v}\rangle \quad , \tag{4.10}$$

and

$$\Sigma_{c'}\langle\bar{v}|c'\rangle \int d\underline{r}\ f_{c'}(\underline{r})\langle\underline{r}|c\rangle = \langle\bar{v}|(-V^I - V^{EL} + \bar{W})|c\rangle \quad . \tag{4.11}$$

At this point in the optimization procedure, Equation (4.10) has commonly been used to suggest a form for the pseudopotential, while Equation (4.11) has been ignored. Since $V^I + V^{EL} = H - T$ and $H|c\rangle = E_c|c\rangle$, we may write Equation (4.10) as

$$\int d\underline{r}\ f_c(\underline{r})\langle\underline{r}|\bar{v}\rangle = \langle c|(T + \bar{W} - E_c)|\bar{v}\rangle \quad . \tag{4.12}$$

In performing a calculation with the pseudopotential, we will want to expand $\bar{v}$ in a set of plane waves. Then we will use perturbation theory to calculate the energy and wavefunction of $\bar{v}$. Therefore, we will need the projection of $f_c(\underline{r})$ on the set of plane waves. Since the set of plane waves is complete, we must know $f_c(\underline{r})$ completely in order to evaluate all of these projections. But Equation (4.12) yields only the projection of $f_c(\underline{r})$ on the single state $\bar{v}$. Accordingly, we must make an assumption regarding that part of $f_c(\underline{r})$ which is left undetermined. The assumption which is most obvious and most commonly made is that $f_c(\underline{r})$ may be given in operator form by

$$f_c(\underline{r}) = (c|\underline{r}\rangle\ (T(\underline{r}) + \bar{W} - E_c) \quad . \tag{4.13}$$

We may note that Expression (4.13) is indeed a local operator, as we imply when we write $f_c(\underline{r})$ as a function of one spatial variable. We may substitute Equation (4.13) into Equation (4.2) to obtain

$$W(\underline{r},\underline{r}') = V^I(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') + \Sigma_c\langle\underline{r}|c\rangle\langle c|\underline{r}'\rangle(T(\underline{r}') + \bar{W} - E_c) \quad . \tag{4.14}$$

This pseudopotential is the optimal pseudopotential most often discussed in calculations involving the pseudopotential method, although approximate forms of Expression (4.14) are often used to simplify calculations [2,3].

If we take the matrix element of Expression (4.14) between two plane waves, $\underline{k}$ and $\underline{k}'$, we may write

$$\langle \underline{k}|W|\underline{k}'\rangle = \langle \underline{k}|V^{I} + V^{EL}|\underline{k}'\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}'\rangle(|\underline{k}'|^2 + \bar{V}_L + \bar{W} - E_c) \quad . \tag{4.15}$$

Expression (4.15) demonstrates that the presence of the operator T in Expression (4.13) makes the pseudopotential non-Hermitian. The non-Hermiticity of Expression (4.14) leads us to question whether or not Expression (4.13) satisfies Equation (4.11) as well as Equation (4.10). If Expression (4.13) does not satisfy Equation (4.11), then it certainly does not specify that $f_c(\underline{r})$ which minimizes $\bar{T}$. If we substitute Expression (4.13) into Equation (4.11), we find that Expression (4.13) cannot possibly minimize $\bar{T}$ unless the following equality is satisfied:

$$\Sigma_{c'} \langle \bar{v}|c'\rangle\langle c'|T|c\rangle \stackrel{?}{=} \langle \bar{v}|T|c\rangle \quad . \tag{4.16}$$

In order to facilitate our discussion of Expression (4.16), let us expand the right-hand side in terms of the complete set of eigenvalues of H to obtain

$$\Sigma_{c'} \langle \bar{v}|c'\rangle\langle c'|T|c\rangle \stackrel{?}{=} \Sigma_{c'} \langle \bar{v}|c'\rangle\langle c'|T|c\rangle + \Sigma_{v'} \langle \bar{v}|v'\rangle\langle v'|T|c\rangle \quad . \tag{4.17}$$

We may cancel the sums over core states which occur on both sides of Expression (4.17). Since $\bar{v}$ may be constructed such that it is

orthogonal to all of the valence states of H except v [1], we may drop all of the remaining terms in Expression (4.17) except one to yield

$$\langle \bar{v}|v\rangle\langle v|T|c\rangle \overset{?}{=} 0 \quad . \tag{4.18}$$

Since it will not generally be true that all of the matrix elements of T between v and the set of core states vanish, we may conclude that Expression (4.13) does not yield a useful form for $f_c(\underline{r})$ which minimizes $\bar{T}$. The failure of Expression (4.13) to satisfy Equation (4.11) stems directly from its inability to predict accurately the projections of $f_c(\underline{r})$ on the set of core states. Since the core states may be expected to have a much greater proportion of high frequency components than $\bar{v}$, we might expect that the failure of Expression (4.13) to minimize $\bar{T}$ will be demonstrated most strongly in the high frequency components of $f_c(\underline{r})$. As we shall demonstrate later, the high frequency behavior of the $f_c(\underline{r})$ given by Expression (4.13) is indeed unsatisfactory.

In any case, Expression (4.14) is certainly a valid pseudopotential in the form of Austin, Heine, and Sham. This expression for the pseudopotential must be evaluated self-consistently since it involves the expectation value of the pseudopotential in the state $\bar{v}$. Accordingly, for calculations on the pseudopotential, it is customary to use various approximations to Expression (4.14). If the state $\bar{v}$ is associated with the point $\underline{k}$ in reciprocal space, Harrison [3] has suggested that the replacement of $\bar{W}$ in Expression (4.14) by $\langle \underline{k}|W|\underline{k}\rangle$ would be a reasonable approximation. The Harrison pseudopotential may then be written as

$$W(\underline{r},\underline{r}') = V^{I}(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') + \Sigma_c \langle \underline{r}|c\rangle\langle c|\underline{r}'\rangle(T(\underline{r}') + \langle \underline{k}|W|\underline{k}\rangle - E_c) \quad . \tag{4.19}$$

This step greatly simplifies the dependence of W on the state $\bar{v}$. It also allows for the self-consistent determination of the pseudopotential through taking the matrix elements of Equation (4.19) between the plane waves $\underline{k}$ and $\underline{k}$. We may solve for $\langle \underline{k}|W|\underline{k}\rangle$, obtaining

$$\langle \underline{k}|W|\underline{k}\rangle = \frac{\langle \underline{k}|V^{I}+V^{EL}|\underline{k}\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2 + \bar{V}_L - E_c)}{1 - \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle} \quad . \tag{4.20}$$

The Harrison pseudopotential, given by Equations (4.19) and (4.20), will be the one used to compare the matrix elements of W derived from Expression (4.14) with those derived by the method we are about to discuss. Two other commonly used pseudopotentials may be obtained from Expression (4.19) by replacing $\langle \underline{k}|W|\underline{k}\rangle$ by either $\langle \underline{k}|V^{I} + V^{EL}|\underline{k}\rangle$ or 0.

Optimization through the Minimization of $\langle \underline{k}|\ (W - \langle \underline{k}|W|\underline{k}\rangle)^2\ |\underline{k}\rangle$

Since the only obvious assumption of a simple form for $f_c(\underline{r})$ from Equation (4.10) does not truly minimize $\bar{T}$, the examination of another optimization procedure might prove more fruitful than an analysis of other possible assumptions. Concerned with optimizing the perturbation expansion in W for the state associated with the point $\underline{k}$ in reciprocal space, Bassani and Celli [4] suggested the minimization of

$$\Sigma'_{\underline{q}} \langle \underline{k}|W|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle \quad . \tag{4.21}$$

The prime on the sum indicates that the term for $\underline{q} = 0$ has been excepted.

We may take advantage of the orthogonality and completeness of the set of plane waves to rewrite Expression (4.21) as

$$\langle \underline{k}| \; (W - \langle \underline{k}|W|\underline{k}\rangle)^2 \; |\underline{k}\rangle \quad . \tag{4.22}$$

Therefore, in minimizing Expression (4.21), we are actually minimizing the mean square deviation of W from the expectation value of the pseudopotential in the state $\underline{k}$. This procedure might be expected to produce a smooth function with a narrow Fourier distribution about $\underline{q} = 0$, which is directly related to the convergence of a perturbation expansion in W. Let us substitute the form of W from Equation (4.2) into Expression (4.21), obtaining

$$\Sigma'_{\underline{q}} \left[\langle \underline{k}|V^I + V^{EL}|\underline{k}+\underline{q}\rangle \; + \Sigma_{c'} \langle \underline{k}|c'\rangle \int d\underline{r} \; f_{c'}(\underline{r}) \langle \underline{r}|\underline{k}+\underline{q}\rangle \right]$$
$$\times \left[\langle \underline{k}+\underline{q}|V^I + V^{EL}|\underline{k}\rangle \; + \Sigma_{c'} \langle \underline{k}+\underline{q}|c'\rangle \int d\underline{r} \; f_{c'}(\underline{r}) \langle \underline{r}|\underline{k}\rangle \right] \quad . \tag{4.23}$$

If we have placed no restrictions upon the form of $f_c(\underline{r})$, we may vary the projection of $f_c(\underline{r})$ on each plane wave independently. Varying the projection of $f_c(\underline{r})$ on the plane wave $\underline{k}$, we obtain

$$\Sigma'_{\underline{q}} \langle \underline{k}|W|\underline{k}+\underline{q}\rangle \langle \underline{k}+\underline{q}|c\rangle = 0 \quad . \tag{4.24}$$

The completeness of the set of plane waves allows us to rewrite Equation (4.24) as

$$\langle \underline{k}|W|c\rangle = \langle \underline{k}|W|\underline{k}\rangle \langle \underline{k}|c\rangle \quad . \tag{4.25}$$

There is an equation like (4.25) for each core state. Similarly, we may vary the projection of $f_c(\underline{r})$ on each plane wave $\underline{k}+\underline{q}$. Setting the

coefficient of each variation equal to zero, we obtain an equation for each $\underline{q} \neq 0$,

$$\langle \underline{k} + \underline{q} | W | \underline{k} \rangle = 0 \quad . \tag{4.26}$$

We may insert the form of W into Equations (4.25) and (4.26) to obtain the following equations for the projections of $f_c(\underline{r})$:

$$\Sigma_{c'} \langle \underline{k} | c' \rangle \int d\underline{r}\, f_{c'}(\underline{r}) \langle \underline{r} | c \rangle = \langle \underline{k} | (-V^I - V^{EL} + \langle \underline{k} | W | \underline{k} \rangle) | c \rangle \tag{4.27}$$

and

$$\Sigma_{c'} \langle \underline{k} + \underline{q} | c' \rangle \int d\underline{r}\, f_{c'}(\underline{r}) \langle \underline{r} | \underline{k} \rangle = \langle \underline{k} + \underline{q} | -V^I - V^{EL} | \underline{k} \rangle \quad . \tag{4.28}$$

We may note immediately that these equations do not involve the projections of $f_c(\underline{r})$ on the set of plane waves $\underline{k+q}$, where $\underline{q} \neq 0$. Therefore, the minimization of Expression (4.23) for a general $f_c(\underline{r})$ does not yield the information which we need to express $f_c(\underline{r})$ in terms of its projections on the set of plane waves. As we noted in connection with our discussion of the other optimization procedure, the use of perturbation theory with a general pseudopotential requires a knowledge of the projections of $f_c(\underline{r})$ on the complete set of plane waves. Further, Expression (4.27) does not appear to contain enough information to determine the projections of the $f_c(\underline{r})$ on the set of core states. Each time a new value of "c" is selected to yield a new equation like Expression (4.27), we introduce a complete new set of projections of the $f_c(\underline{r})$ on the new core state. Accordingly, we will always have more variables than constraining equations. Thus the

minimization of Expression (4.23) for a general $f_c(\underline{r})$ does not yield the projections of $f_c(\underline{r})$ either on the set of core states or on the set of plane waves $\underline{k+q}$, where $\underline{q} \neq 0$. We shall now demonstrate through contradiction that Equation (4.28) over-constrains the projection of $f_c(\underline{r})$ on the plane wave $\underline{k}$. If we assume that Equation (4.26) holds for each value of $\underline{q} \neq 0$, we may multiply it by $\langle v|\underline{k}+\underline{q}\rangle$ and sum over all values of $\underline{q} \neq 0$, yielding

$$\Sigma'_{\underline{q}} \langle v|\underline{k}+\underline{q}\rangle\langle \underline{k}+\underline{q}|W|\underline{k}\rangle = 0 \quad . \tag{4.29}$$

Taking advantage of the completeness of the set of plane waves, we can rewrite (4.29) as

$$\langle v|W|\underline{k}\rangle = \langle v|\underline{k}\rangle\langle \underline{k}|W|\underline{k}\rangle \quad . \tag{4.30}$$

Since v is an eigenstate of H, it is orthogonal to all members of the set of core states. Accordingly, we may insert the form of W into the left-hand side of Equation (4.30) to obtain

$$\langle v|V^I + V^{EL}|\underline{k}\rangle = \langle v|\underline{k}\rangle\langle \underline{k}|W|\underline{k}\rangle \quad . \tag{4.31}$$

By definition, each state v has an eigenvalue E_v such that

$$\langle v|\ (H - E_v)\ |\underline{k}\rangle = 0 \quad . \tag{4.32}$$

We may now let $H = T + V^I + V^{EL}$ and substitute from Equation (4.31) into the resulting equation to obtain

$$(|\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|W|\underline{k}\rangle - E_v)\langle v|\underline{k}\rangle = 0 \quad . \tag{4.33}$$

Even in an ordered alloy, there will be many valence states for which $\langle v|\underline{k}\rangle$ does not vanish. According to Equation (4.33), all of these

states must have the same eigenvalues. But the Austin, Heine, and Sham form of the pseudopotential has been shown to yield the correct eigenvalues for all valence states [1]. Since these eigenvalues can not all be identical, the Austin, Heine, and Sham form of the pseudopotential must not be able to satisfy Equation (4.26) for all values of $\underline{q} \neq 0$. Thus we have demonstrated through contradiction that Equation (4.28) over-constrains the projection of $f_c(\underline{r})$ on the plane wave $\underline{k}$, if it is taken to hold for all $\underline{q} \neq 0$. Since we are seeking a well-defined procedure for selecting an optimal pseudopotential, we do not want to select certain arbitrary values of $\underline{q}$ for which Equation (4.28) must hold. In summary, we have found that the minimization of Expression (4.21) for a general pseudopotential does not yield the projections of $f_c(\underline{r})$ on plane waves which we need for a perturbation expansion.

Let us apply some logical constraint upon the form of W in an attempt to obtain an optimal pseudopotential from the minimization of Expression (4.21). We will seek that Hermitian pseudopotential which minimizes Expression (4.21), relative to other Hermitian pseudopotentials. We may now write Expression (4.21) so that it involves only the projection of $f_c(\underline{r})$ of the plane wave $\underline{k}$ to obtain

$$\Sigma'_{\underline{q}} \left| \langle \underline{k}+\underline{q} | V^{I}+V^{EL} | \underline{k} \rangle + \Sigma_{c'} \langle \underline{k}+\underline{q} | c' \rangle \int d\underline{r}\ f_{c'}(\underline{r}) \langle \underline{r} | \underline{k} \rangle \right|^2 \quad . \tag{4.34}$$

We will vary independently the projection of $f_c(\underline{r})$ on the plane wave $\underline{k}$ and the complex conjugate of that projection. Proceeding as before, we obtain the following two conditions:

$$\langle \underline{k}|W|c\rangle = \langle \underline{k}|W|\underline{k}\rangle\langle \underline{k}|c\rangle \quad , \tag{4.35}$$

and

$$\langle c|W|\underline{k}\rangle = \langle c|\underline{k}\rangle\langle \underline{k}|W|\underline{k}\rangle \quad . \tag{4.36}$$

We may note the marked similarity between this pair of equations and the pair, (4.8) and (4.9). In the earlier case, however, we were able to deduce one member of the pair from the other using the Hermiticity of T. This time we had to restrict W to being Hermitian to obtain both members of the pair. If we substitute the form of W into the left-hand sides of these two equations, we may write

$$\Sigma_{c'}\langle \underline{k}|c'\rangle \int d\underline{r}\ f_{c'}(\underline{r})\langle \underline{r}|c\rangle = \langle \underline{k}|(-V^{I}-V^{EL}+\langle \underline{k}|W|\underline{k}\rangle)|c\rangle \quad , \tag{4.37}$$

and

$$\int d\underline{r}\ f_c(\underline{r})\langle \underline{r}|\underline{k}\rangle = \langle c|\ (-V^{I}-V^{EL}+\langle \underline{k}|W|\underline{k}\rangle)\ |\underline{k}\rangle \quad . \tag{4.38}$$

There are two obvious forms for $f_c(\underline{r})$ which we may deduce from Equation (4.38). Using the property that the plane waves are eigenfunctions of T, we may write the two possibilities as

$$f_c(\underline{r}) = \langle c|\underline{r}\rangle(T(\underline{r}) + \langle \underline{k}|W|\underline{k}\rangle - E_c) \quad , \tag{4.39}$$

and

$$f_c(\underline{r}) = \langle c|\underline{r}\rangle(|\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|W|\underline{k}\rangle - E_c) \quad . \tag{4.40}$$

The first possibility is similar to Expression (4.13). As we noted in this earlier case, the presence of the operator T makes the resulting pseudopotential non-Hermitian. Since we have restricted W to be Hermitian in this treatment, Expression (4.39) is clearly not a suitable solution. However, we may substitute Expression (4.40) into the form of W to obtain

$$W(\underline{r},\underline{r}') = V^{I}(\underline{r},\underline{r}') + V^{EL}(\underline{r},\underline{r}') + \Sigma_c \langle \underline{r}|c\rangle(|\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|W|\underline{k}\rangle - E_c)\langle c|\underline{r}'\rangle \ . \tag{4.41}$$

This pseudopotential is obviously Hermitian. Accordingly, we know that Equation (4.40) must satisfy Equation (4.35) as well as Equation (4.36).* We should not state that Expression (4.41) is the Hermitian pseudopotential which minimizes Expression (4.21), but rather that the projection of Expression (4.41) on the state $\underline{k}$ is equal to the projection on $\underline{k}$ of that Hermitian pseudopotential which minimizes Expression (4.21). In order to find the optimal projections of $f_c(\underline{r})$ on the set of plane waves $\underline{k+q}$, for $\underline{q} \neq 0$, we must leave these projections in our form of Expression (4.21). But now we cannot vary the projections of $f_c(\underline{r})$ on each plane wave independently since we have constrained the resulting W to be Hermitian. There does not appear to be any well-defined procedure for obtaining these optimal projections for the Hermitian pseudopotential which minimizes Expression (4.21). However, if we are interested in using no more than second order in perturbation theory to find the electronic energies, we do not need the projection of $f_c(\underline{r})$ on any plane wave other than $\underline{k}$.

In summary, we have established a well-defined procedure for finding the projection on the plane wave $\underline{k}$ of that Hermitian pseudopotential which minimizes Expression (4.21). To second order in a perturbation expansion in W, that optimal pseudopotential will have the same conduction electron eigenvalues as the pseudopotential given by Equation (4.41). Since the optimal pseudopotential and the

*Harrison has shown that the eigenfunctions of this pseudopotential are the eigenfunctions of the actual crystalline potential.

pseudopotential of Equation (4.41) are both valid pseudopotentials in the Austin, Heine, and Sham form, we also know that they must yield the same conduction electron energies when solved exactly. Expression (4.41) may be evaluated self-consistently by taking its matrix element between the plane waves, $\underline{k}$ and $\underline{k}$. We may then express $\langle \underline{k}|W|\underline{k}\rangle$ by

$$\langle \underline{k}|W|\underline{k}\rangle = \frac{\langle \underline{k}|V^{I} + V^{EL}|\underline{k}\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2 + \bar{V}_L - E_c)}{1 - \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle} \quad . \tag{4.42}$$

We may now substitute Equation (4.42) into Equation (4.41) to obtain a self-consistent expression for the pseudopotential.

Comparison Between the Two Pseudopotentials

On the preceding pages, we have derived two different pseudopotentials, given by Equations (4.19) and (4.41). Both of these forms are valid pseudopotentials in that they satisfy the Austin, Heine, and Sham form. The former pseudopotential has not been shown to satisfy exactly the condition of minimizing $\bar{T}$, but is commonly used in calculations. The latter pseudopotential has been shown to yield the same eigenvalues to second order in perturbation theory as that Hermitian pseudopotential which minimizes Expression (4.21). The final test of a pseudopotential is its performance in augmenting the convergence of a perturbation expansion. In Figures 4.[illegible] through 4.6, we have graphed the matrix elements of the average and difference

screened pseudopotentials, as discussed in Chapter Two, between the plane waves $\underline{k}$ and $\underline{k+q}$ for the 50-50 alloy of lithium-magnesium. We have labeled the matrix elements of Equation (4.41) as the present pseudopotential (P.P.) and those of Equation (4.19) as the Harrison pseudopotential (P.P.). Not only does the present pseudopotential have the advantage of being Hermitian, but its matrix elements go more smoothly to zero as $\underline{q}$ becomes large than do the matrix elements of the Harrison pseudopotential. Since the radius of the Fermi sphere corresponds to about 0.67 atomic units in reciprocal space, we would like to cut off the sum over $\underline{q}$ which occurs in perturbation theory once the magnitude of $\underline{q}$ exceeds five or six atomic units. If we do not cut off the sum in this way, the summation becomes very tedious. We might have confidence that the error introduced by this cut-off in a summation using the present pseudopotential is less than in the case of the Harrison pseudopotential. In addition, the smaller width of the present pseudopotential in reciprocal space suggests that the error introduced by neglecting higher order terms in perturbation theory will be smaller than in the case of the Harrison pseudopotential. The greater magnitude of the Harrison pseudopotential for large $\underline{q}$ results directly from the presence of T in the pseudopotential. As we noted previously, this unfortunate behavior for large $\underline{q}$ might have been expected from the inability of this pseudopotential to satisfy Equation (4.9). In any case, the behavior of the matrix elements suggests that the pseudopotential of Equation (4.41) would be more suitable for calculations than the pseudopotential of Equation (4.19).

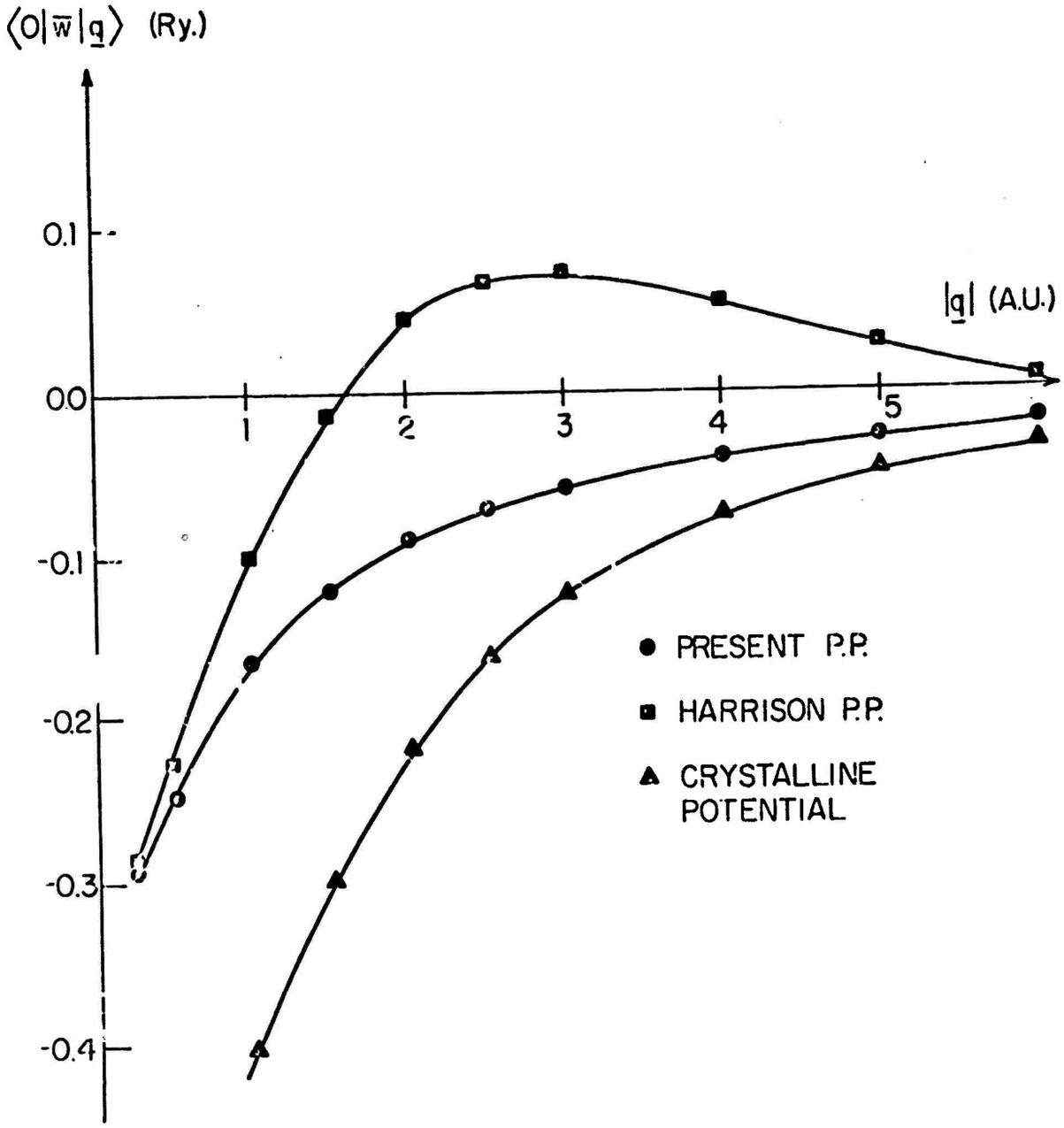

FIG. 4-1 $\langle \underline{k}|\bar{w}|\underline{k}+\underline{q}\rangle$ FOR $\underline{k} = 0.0\hat{x}$, $\underline{q} = |\underline{q}|\,\hat{x}$

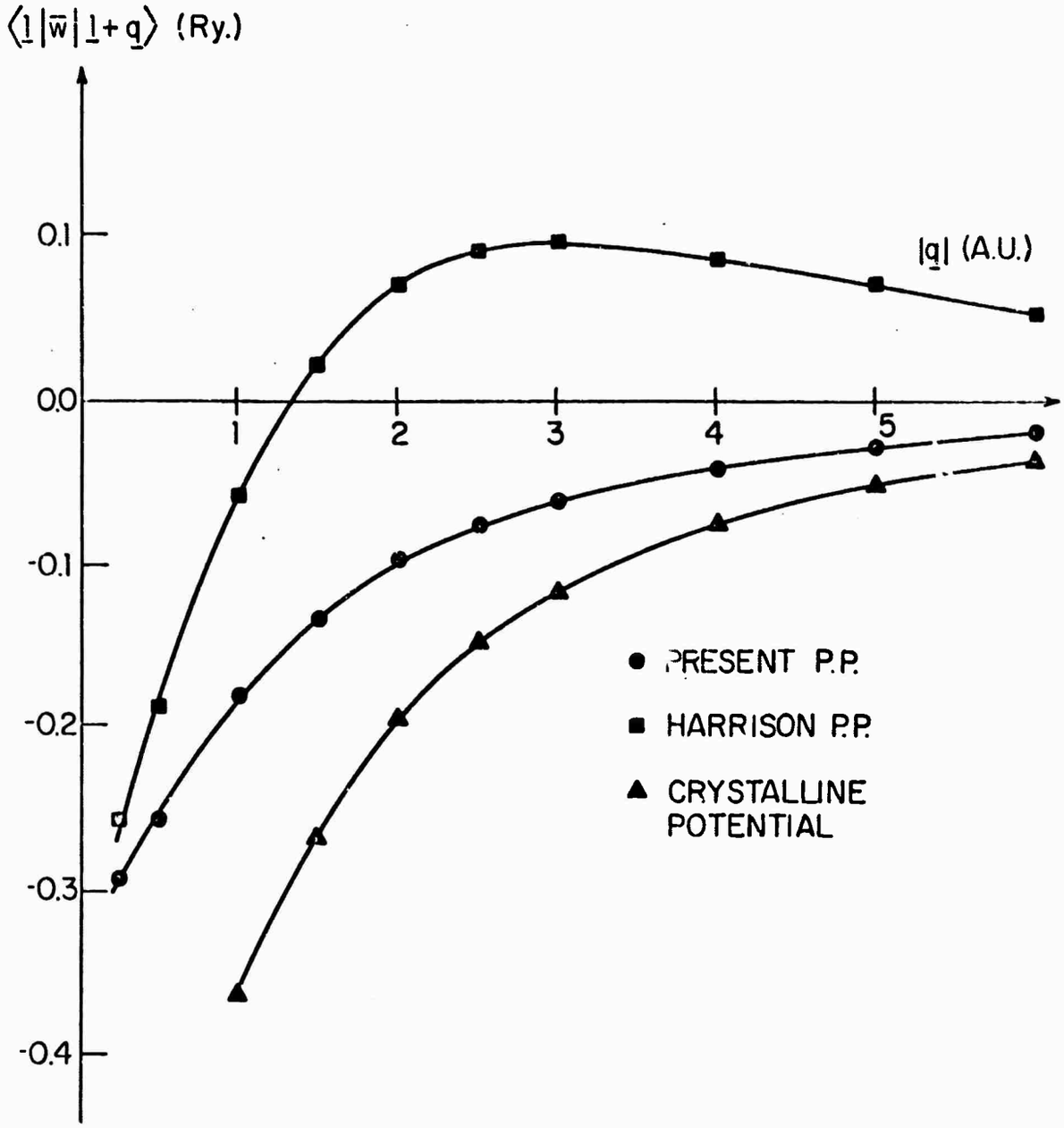

FIG. 4-2 $\langle \underline{k}|\bar{w}|\underline{k}+\underline{q}\rangle$ FOR $\underline{k} = 1.0\hat{x}$, $\underline{q} = |\underline{q}|\hat{x}$

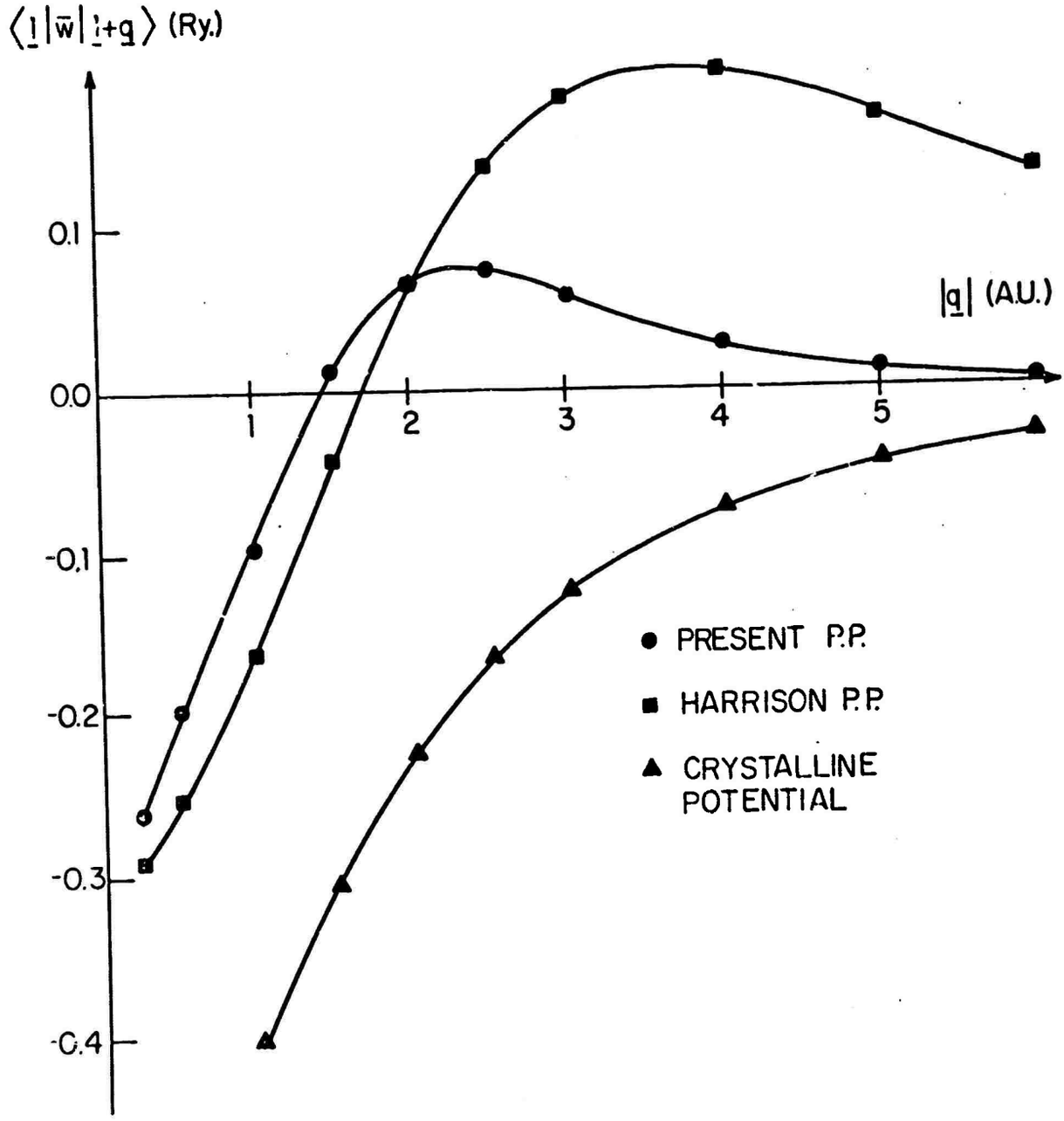

FIG. 4-3 $\langle \underline{k} | \bar{w} | \underline{k}+\underline{q} \rangle$ FOR $\underline{k} = 1.0\hat{x}$, $\underline{q} = -|\underline{q}|\hat{x}$

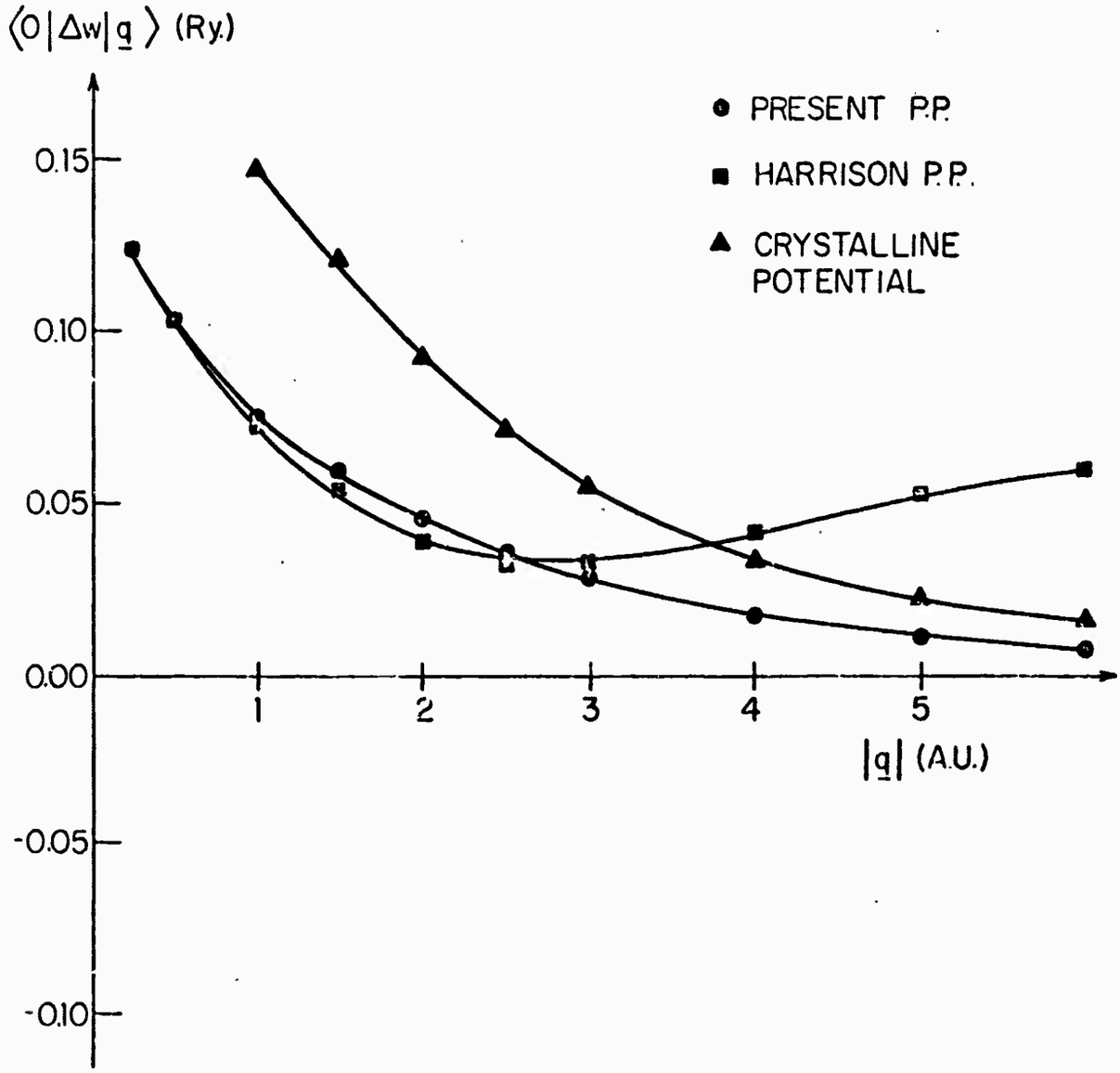

FIG. 4-4 $\langle \underline{k} | \Delta w | \underline{k}+\underline{q} \rangle$ FOR $\underline{k} = 0.0\hat{x}$, $\underline{q} = |\underline{q}|\hat{x}$

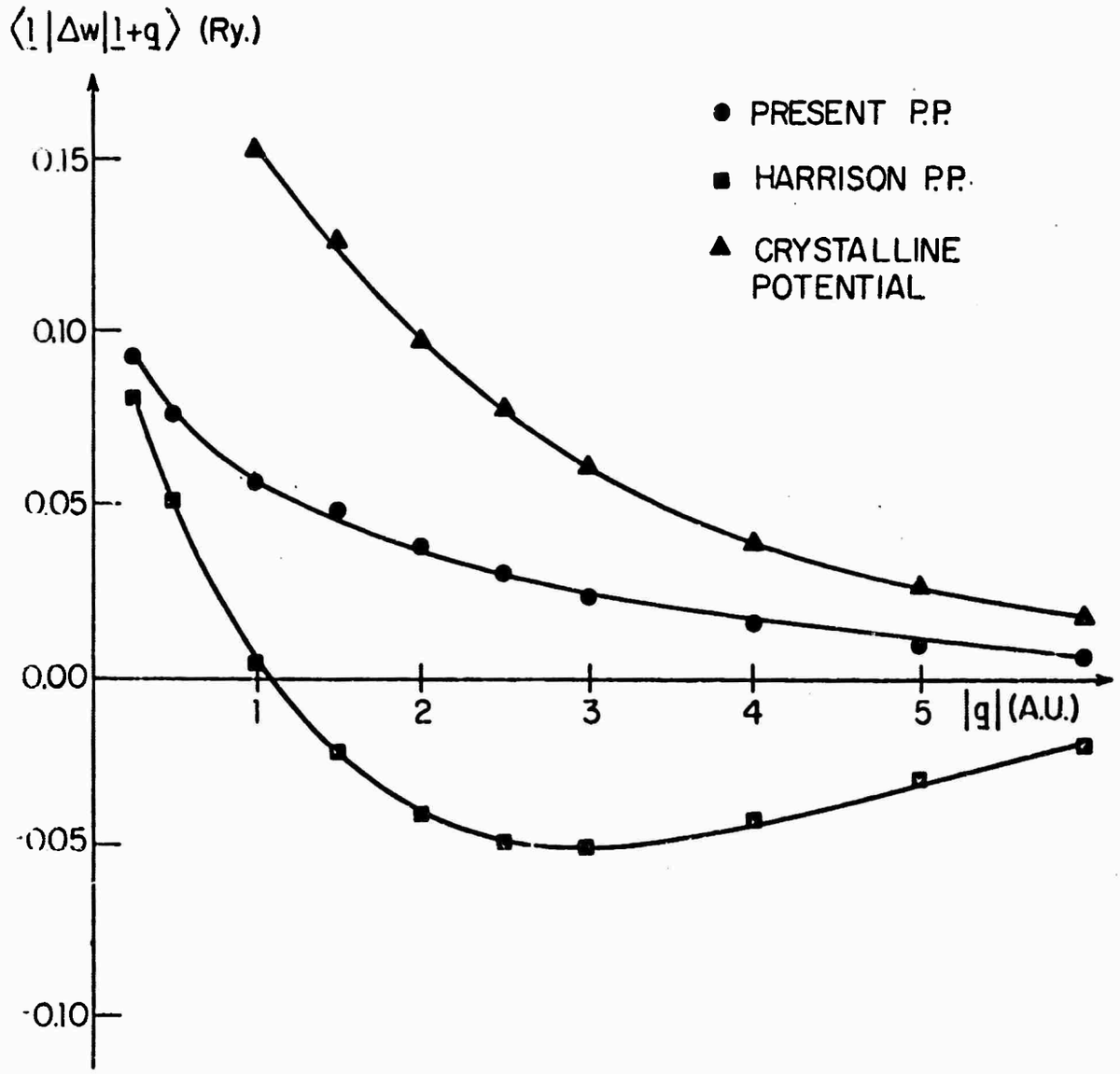

FIG. 4-5 $\langle \underline{k}|\Delta w|\underline{k}+\underline{q}\rangle$ FOR $\underline{k} = 1.0\hat{k}$, $\underline{q} = |\underline{q}|\hat{x}$

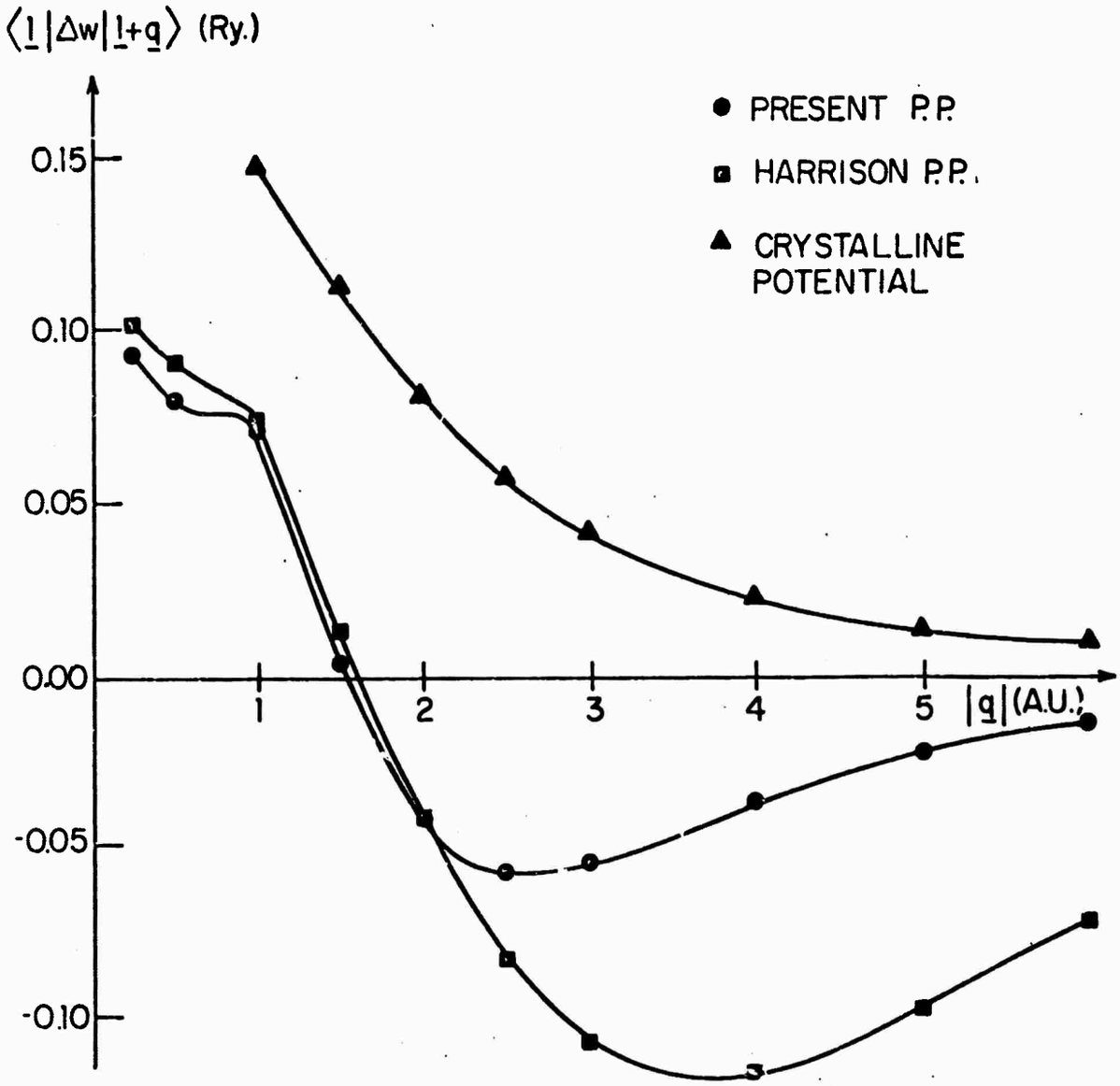

FIG. 4-6 $\langle \underline{k}|\Delta w|\underline{k}+\underline{q}\rangle$ FOR $\underline{k} = 1.0\hat{x}$, $\underline{q} = -|\underline{q}|\hat{x}$

Comparison with the Phillips and Kleinman Pseudopotential

While not central to the purpose of this work, it might be interesting to compare the pseudopotential of Equation (4.41) with the well-known Hermitian pseudopotential of Phillips and Kleinman [5,6]. They rearranged the terms in the OPW secular equation to place it in a form similar to that of the Austin, Heine and Sham pseudopotential. $f_c(\underline{r})$ is then given by

$$f_c(\underline{r}) = \langle c|\underline{r}\rangle(E_v - E_c) \quad . \tag{4.43}$$

Since this expression involves the energy, E_v, of the state in which we are interested, we must use some self-consistent procedure to calculate eigenvalues from the Phillips and Kleinman pseudopotential. However, if we are to form a valid comparison between this pseudopotential and that of Equation (4.41), we should calculate the energies from Equation (4.43) under the conditions for which Equation (4.41) is rigorously optimal. Therefore, we shall evaluate the electronic eigenvalues from Equation (4.43) to second order in the pseudopotential.

To second order in the pseudopotential, we may write the energy of the electronic state v associated with the point $\underline{k}$ in reciprocal space in terms of a Hermitian pseudopotential as

$$E_v = |\underline{k}|^2 + \bar{V}_L + \langle \underline{k}|W|\underline{k}\rangle + \Sigma'_{(\underline{q})} \frac{|\langle \underline{k}|W|\underline{k}+\underline{q}\rangle|^2}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \quad . \tag{4.44}$$

When we are considering the order of the various terms in Equation (4.44) which arise from the insertion of the Phillips and Kleinman

pseudopotential, we may choose whether to regard $\Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle$ as being actually of zero'th order in the pseudopotential or as being effectively of first order. As we noted in connection with our discussion of the screening potential in Chapter Two, this sum over the core states is usually of order 0.1. Accordingly, it is reasonable to consider it as being comparable with a first order expression in W. Let us do so, and expand E_v in powers of λ, where λ is the strength of the pseudopotential. We may now write the Phillips and Kleinman pseudopotential as

$$W = \lambda(V^I + V^{EL} + \Sigma_c \; |c\rangle(E_v^{(0)} - E_c)\langle c|) + \lambda^2 \, E_v^{(1)} \, \Sigma_c |c\rangle\langle c| + \lambda^3 \, E_v^{(2)} \, \Sigma_c |c\rangle\langle c| + \cdots \quad . \tag{4.45}$$

We may now insert Equation (4.45) into Equation (4.44) and expand the left-hand side of Equation (4.44) in powers of λ. If we then demand that the equality hold for coefficients of each power of λ, we may write

$$E_v^{(0)} = |\underline{k}|^2 + \bar{V}_L \quad , \tag{4.46}$$

$$E_v^{(1)} = \langle \underline{k}|V^I + V^{EL}|\underline{k}\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(E_v^{(0)} - E_c) \tag{4.47}$$

and

$$E_v^{(2)} = E_v^{(1)} \, \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle + \Sigma'_{\{\underline{q}\}} \frac{|\langle \underline{k}|V^I + V^{EL}|\underline{k}+\underline{q}\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}+\underline{q}\rangle(E_v^{(0)} - E_c)|^2}{|\underline{k}|^2 - |\underline{k}+\underline{q}|^2} \quad . \tag{4.48}$$

Considering now the pseudopotential of Equation (4.41), we may again consider that $\Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle$ is of first-order in the pseudopotential.

Hence, the diagonal matrix element of W in Equation (4.42) may be written in powers of λ as

$$\langle \underline{k}|W|\underline{k}\rangle = \lambda(\langle \underline{k}|V^{I} + V^{EL}|\underline{k}\rangle - \Sigma_c\langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2 + \bar{V}_L - E_c))$$
$$+ \lambda^2\Sigma_c\langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(\langle \underline{k}|V^{I}+V^{EL}|\underline{k}\rangle - \Sigma_c\langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2+\bar{V}_L-E_c))$$
$$+ \cdots \quad . \tag{4.49}$$

If we substit[illegible] this expression into Equation (4.41) and substitute Equation (4.4[illegible] to Equation (4.44), we may follow the procedure outlined above to obtain a set of three equations identical to Equations (4.46), (4.47), and (4.48). Accordingly, the Phillips and Kleinman pseudopotential yields the same eigenvalues to second order in the pseudopotential as Equation (4.41) if we may consider $\Sigma_c\langle \underline{k}|c\rangle\langle c|\underline{k}\rangle$ as being of first order in W. If we may not consider this sum over core states as being of first-order in the pseudopotential, then the electronic eigenvalues obtained to second order through the two methods differ by about 10% in the second order term. Accordingly, we may state that the second-order perturbation theory electronic energies obtained through the Phillips and Kleinman pseudopotential and through Equation (4.41) differ by no more than about 10% in the second order term.

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Chapter Five

AN ALLOY CALCULATION USING THE PSEUDOPOTENTIAL METHOD

Having completed our formal discussion of the application of the pseudopotential method to the alloy problem, we will now describe the procedure to be followed in performing an actual calculation. For this purpose, we will use the Hermitian pseudopotential which we discussed in Chapter Four. We will calculate the total conduction electron contribution to the ordering energy and the effective pairwise interaction between the ions. In both instances, we will evaluate the electronic energies only to second order in perturbation theory. Accordingly, we may write the matrix elements of that pseudopotential which are appropriate for this calculation of the properties of the electronic state associated with $\underline{k}$ as

$$\langle \underline{k}+\underline{q}|W|\underline{k}\rangle = \langle \underline{k}+\underline{q}|V^{I}+V^{EL}|\underline{k}\rangle + \Sigma_c \langle \underline{k}+\underline{q}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2+\bar{V}_L+\langle \underline{k}|W|\underline{k}\rangle - E_c) \tag{5.1}$$

where

$$\langle \underline{k}|W|\underline{k}\rangle = \frac{\langle \underline{k}|V^{I}+V^{EL}|\underline{k}\rangle + \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle(|\underline{k}|^2+\bar{V}_L - E_c)}{1-\Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle} \quad . \tag{5.2}$$

We must evaluate these matrix elements for all values of $\underline{k}$ within the Fermi sphere and, in principle, for all values of $\underline{q}$. We have assumed that the wavefunctions of the core states involved in the sum over "c" are independent of the crystalline environment of the ion with which they are associated. For calculational purposes, we

shall further assume that these core wavefunctions may be closely approximated with the wavefunctions of the corresponding states of the neutral atom. We have chosen the neutral atom for this correspondence since we expect that the conduction electron density in the region of the core is best approximated by the valence states of the neutral atom. The analytic atomic Hartree-Fock wavefunctions calculated by E. Clementi [1] will be used for this purpose.

As we discussed in Chapter Two, the screening contribution to the matrix elements of W depends upon a knowledge of the unscreened pseudopotential. Accordingly, we must calculate the matrix elements of the unscreened pseudopotential before we can calculate the screening potential. The unscreened pseudopotential consists of the crystalline ionic potential, denoted by V^I, plus the sum over core states as in Equation (5.1). We shall first consider the matrix elements of V^I.

Matrix Elements of the Ionic Potential

As we demonstrated in Chapter Two, the matrix elements of the pseudopotential may be separated, with certain approximations, into a structure-dependent factor and a second factor which depends upon the structure for a given ionic volume only through $f_c(\underline{r})$. The structure-dependent factor is either a Kronecker delta or $F(\underline{q})$, the properties of which we discussed in Chapter Three. Accordingly, we shall consider in this chapter the evaluation of the second factor in the pseudopotential. The contribution of this factor to V^I depends

upon the matrix elements of the Hartree-Fock potentials of the individual ions. This ionic potential may be written for an ion of type i as

$$v_i(\underline{r},\underline{r}') = \frac{2Z}{|\underline{r}|}\,\delta(\underline{r}-\underline{r}') - 2\,\Sigma_c \int d\underline{r}''\,\frac{\langle \underline{r}''|c\rangle\langle c|\underline{r}''\rangle}{|\underline{r}-\underline{r}''|}\,\delta(\underline{r}-\underline{r}')$$

$$+\,2\,\Sigma_c\,\frac{\langle \underline{r}|c\rangle\langle c|\underline{r}'\rangle}{|\underline{r}-\underline{r}'|}\,, \tag{5.3}$$

where the sums over "c" extend over all the core states associated with the ion in question. We wish to multiply this potential by $\langle \underline{k}+\underline{q}|\underline{r}\rangle$ and $\langle \underline{r}'|\underline{k}\rangle$, and then integrate the product over all values of $\underline{r}$ and $\underline{r}'$ within the crystal. This integral is then multiplied by the total number of ions in the crystal, denoted by N, to obtain $\langle \underline{k}+\underline{q}|v_i|\underline{k}\rangle_{\Omega_0}$.

Our discussion of the matrix elements of Equation (5.3) will be facilitated by an expression for $1/|\underline{r}|$ expanded in the set of plane waves. We may write $1/|\underline{r}|$ as

$$\frac{1}{|\underline{r}|} = \Sigma_{\{\underline{q}\}}\, A_{\underline{q}}\, e^{i\underline{q}\cdot\underline{r}}\,. \tag{5.4}$$

We may multiply both sides of Equation (5.4) by $\exp(-i\underline{q}'\cdot\underline{r})$ and integrate over all values of $\underline{r}$ to obtain

$$A_{\underline{q}'} = \frac{1}{\Omega}\int d\underline{r}\,\frac{e^{-i\underline{q}'\cdot\underline{r}}}{|\underline{r}|}\,. \tag{5.5}$$

In order to evaluate this integral, we must limit the range of the

function $1/|\underline{r}|$ by multiplying by $\exp(-a|\underline{r}|)$. We may then evaluate the integral as "a" approaches zero to obtain the following expansion for $1/|\underline{r}|$:

$$\frac{1}{|\underline{r}|} = \frac{4\pi}{\Omega} \Sigma_{\{\underline{q}\}} \frac{e^{i\underline{q}\cdot\underline{r}}}{|\underline{q}|^2} \quad . \tag{5.6}$$

Using this expansion for $1/|\underline{r}|$, we may write the matrix element of the first term in Equation (5.3) as

$$\frac{2Z}{\Omega_o} 4\pi \Sigma_{\{\underline{q}'\}} \int d\underline{r} \frac{e^{-i\underline{q}\cdot\underline{r}}}{\Omega} \frac{e^{i\underline{q}'\cdot\underline{r}}}{|\underline{q}'|^2} \quad . \tag{5.7}$$

The orthonormality of the set of plane waves allows us to write the matrix element of the first term in Equation (5.3) as

$$\frac{8\pi Z}{\Omega_o} \frac{1}{|\underline{q}|^2} \quad . \tag{5.8}$$

Considering the matrix element of the second term in Equation (5.3), we may expand $1/|\underline{r}-\underline{r}''|$ using Equation (5.6). We may again use the orthonormality of the set of plane waves to write this matrix element as

$$-2 \Sigma_c \int d\underline{r}'' \langle \underline{r}''|c\rangle\langle c|\underline{r}''\rangle \frac{4\pi}{\Omega_o} \frac{e^{-i\underline{q}\cdot\underline{r}''}}{|\underline{q}|^2} \quad . \tag{5.9}$$

Now we must consider the sum over the core states which occurs in this integrand. The analytic core wavefunctions are given by Clementi in the form

$$\langle \underline{r}|n\ell ms\rangle = R_{n\ell}(|\underline{r}|)\, Y_\ell^m(\theta_{\underline{r}},\varphi_{\underline{r}})g(s) \tag{5.10}$$

where

$$R_{n\ell}(|\underline{r}|) = \Sigma_{\bar{n}j} D_{\substack{n\ell \\ \bar{n}j}} \frac{(2\zeta_{\bar{n}j\ell})^{\bar{n}+\frac{1}{2}}}{[(2\bar{n})!]^{\frac{1}{2}}} \; |\underline{r}|^{\bar{n}-1} \; e^{-\zeta_{\bar{n}j\ell}|\underline{r}|} \quad . \tag{5.11}$$

For a given element, all of the atomic wavefunctions with given values of "n" and "ℓ" have the same radial distribution of charge density. We would then expect that the set of core states for that element will include states with all values of "m" and "s" for each pertinent value of "n" and "ℓ". In other words, each shell, as specified by "n" and "ℓ", is filled. Therefore, we may write Expression (5.9) as

$$- \frac{16\pi}{\Omega_o} \frac{1}{|\underline{q}|^2} \Sigma_{n\ell} \int d\underline{r}'' |R_{n\ell}(|\underline{r}''|)|^2 \Sigma_{m=-\ell}^{+\ell} |Y_\ell^m(\theta_{\underline{r}''}, \varphi_{\underline{r}''})|^2 \; e^{-i\underline{q}\cdot\underline{r}''} . \tag{5.12}$$

But, we may take advantage of the relation,

$$\Sigma_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta_{\underline{r}}, \varphi_{\underline{r}}) \; Y_\ell^m(\theta_{\underline{r}'}, \varphi_{\underline{r}'}) = \frac{2\ell+1}{4\pi} P_\ell(\cos \theta_{\underline{r},\underline{r}'}) \quad , \tag{5.13}$$

to note that the core wavefunctions contribute only a spherically symmetric factor to the integrand. We may expand the exponential factor in Expression (5.12) in terms of spherical Bessel functions and spherical harmonics using

$$e^{i\underline{q}\cdot\underline{r}} = 4\pi \Sigma_{\ell=0}^{\infty} (i)^\ell \; j_\ell(|\underline{q}| \; |\underline{r}|) \; \Sigma_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta_{\underline{q}}, \varphi_{\underline{q}}) \; Y_\ell^m(\theta_{\underline{r}}, \varphi_{\underline{r}}) \; . \tag{5.14}$$

If we substitute Equations (5.13) and (5.14) into Expression (5.12), we may perform the angular integrations and use the orthonormality of the set of spherical harmonics to write the matrix element of the second term in Equation (5.3) as

$$- \frac{16\pi}{\kappa_0} \frac{1}{|\underline{q}|^2} \Sigma_{n\ell}(2\ell+1)\int_0^\infty d|\underline{r}''| \; |\underline{r}''|^2 \; |R_{n\ell}(|\underline{r}''|)|^2 j_0(|\underline{q}| \; |\underline{r}''|) \; . \quad (5.15)$$

This integral may be evaluated readily once we note that

$$j_0(|\underline{q}| \; |\underline{r}''|) = \frac{\sin(|\underline{q}| \; |\underline{r}''|)}{|\underline{q}| \; |\underline{r}''|} \; . \quad (5.16)$$

From the form of $R_{n\ell}$ given in Equation (5.11), we see that all of the integrals represented in (5.15) fall into the general class whose values are given by

$$\int_0^\infty dx \; x^n \; e^{-Ax} \sin Bx = \frac{n! \; \mathrm{IM}[(A+iB)^{n+1}]}{(A^2+B^2)^{n+1}} \; . \quad (5.17)$$

Equations (5.16) and (5.17) allow us to readily evaluate Expression (5.15). Accordingly, we have obtained closed forms for the matrix elements between plane waves of both the first and second terms in Equation (5.3).

An examination of the third term in Equation (5.3) reveals that the matrix elements of the Fock exchange potential may not be expressed simply in closed form. We shall seek a form for these matrix elements which may be treated in a direct manner using standard programming techniques. The integrals over real space, as given by

$$2N \; \Sigma_c \int d\underline{r} \int d\underline{r}' \; \frac{\langle \underline{k}+\underline{q}|\underline{r}\rangle\langle \underline{r}|c\rangle\langle c|\underline{r}'\rangle\langle \underline{r}'|\underline{k}\rangle}{|\underline{r}-\underline{r}'|} \; , \quad (5.18)$$

would be difficult to evaluate using a computer due to the vanishing of the denominator at infinitely [illegible] points in the double integral. As an alternative, we might consider expanding the denominator in Expression (5.18) using

$$\frac{1}{|\underline{r}-\underline{r}'|} = \Sigma_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_{\ell}(\cos\theta_{\underline{r},\underline{r}'}) \quad . \tag{5.19}$$

We may now express the exponentials and the core states in Expression (5.18) in terms of spherical harmonics. The angular integrals of products of three spherical harmonics may be treated using the formalism described by Condon and Shortley [2]. The final form of the matrix element involves two coupled integrations over real space and an infinite sum over values of the angular momentum quantum number. This form is also not easily evaluated using a computer.

A simple form for the matrix elements of the Fock potential may be obtained by expanding $1/|\underline{r}-\underline{r}'|$ in terms of plane waves. Since we may not take advantage of the orthonormality of the plane waves to select one plane wave from this expansion, we will find it convenient to express Equation (5.6) in terms of an integral. The density of points in reciprocal space is $\Omega/(2\pi)^3$. Accordingly, we may write Equation (5.6) as

$$\frac{1}{|\underline{r}|} = \frac{1}{2\pi^2} \int d\underline{q} \, \frac{e^{i\underline{q}\cdot\underline{r}}}{|\underline{q}|^2} \quad . \tag{5.20}$$

If we express the denominator in Expression (5.18) using Equation (5.20), we have separated the two integrals over real space. This step greatly simplifies the integration by computer. We may now write Expression (5.18) as

$$\frac{N}{\pi^2} \int d\underline{q}' \, \frac{1}{|\underline{q}'|^2} \langle \underline{k}+\underline{q}+\underline{q}'|c\rangle\langle c|\underline{k}+\underline{q}'\rangle \quad . \tag{5.21}$$

We need only evaluate the projection of a core state on each member of the set of plane waves. This projection may be written using Equation (5.10) as

$$\langle \underline{q}|n\ell ms\rangle = \int d\underline{r}\, \frac{e^{-i\underline{q}\cdot\underline{r}}}{\sqrt{\Omega}}\, R_{n\ell}(|\underline{r}|)\, Y_\ell^m(\theta_{\underline{r}}, \varphi_{\underline{r}}) \quad , \tag{5.22}$$

where both the plane wave and the core state must have the same spin quantum numbers. We may expand the plane wave using Equation (5.14) and perform the angular integration to obtain

$$\langle \underline{q}|n\ell ms\rangle = \frac{4\pi(i)^\ell}{\sqrt{\Omega}}\, Y_\ell^m(\theta_{\underline{q}}, \varphi_{\underline{q}}) \int d|\underline{r}|\; |\underline{r}|^2\, R_{n\ell}(|\underline{r}|)\, j_\ell(|\underline{q}|\;|\underline{r}|). \tag{5.23}$$

The spherical Bessel functions may be expressed in terms of the following recursion formula:

$$j_\ell(x) = \left[x^\ell\left(-\frac{1}{x}\frac{d}{dx}\right)^\ell\right] j_0(x) \quad . \tag{5.24}$$

Therefore, the integrals over $|\underline{r}|$ in Equation (5.23) are of a form to be evaluated using either Equation (5.17) or

$$\int dx\, x^n\, e^{-Ax} \cos Bx = \frac{n!\; \mathrm{RE}[(A+iB)^{n+1}]}{(A^2+B^2)^{n+1}} \quad . \tag{5.25}$$

We may now perform the sum over "m" and "s" in Expression (5.21). Since the spins of the plane wave states and the core states must be the same in each term in this case, we do not get a factor of two from the spin summation as we did in obtaining Expression (5.12). We may use Equation (5.13) to write the matrix element of the third term in Equation (5.3) as

$$\frac{4}{\pi\Omega_o}\Sigma_{n\ell}(2\ell+1)\int dq'\ P_\ell(\cos\theta_{\underline{k+q+q'},\underline{k+q'}})$$
$$\times\int d|\underline{r}|\ |\underline{r}|^2\ R_{n\ell}(|\underline{r}|)\ j_\ell(|\underline{k}+\underline{q}+\underline{q}'|\ |\underline{r}|)$$
$$\times\int d|\underline{r}'|\ |\underline{r}'|^2 R_{n\ell}(|\underline{r}'|)j_\ell(|\underline{k}+\underline{q}'|\ |\underline{r}'|)\ . \qquad (5.26)$$

Thus we have obtained an expression for the matrix element of the Fock potential which may be evaluated in a direct manner.

We have all the information which we need to evaluate $\langle\underline{k}+\underline{q}|v_i|\underline{k}\rangle_{\Omega_o}$ from the analytic atomic wavefunctions of Clementi. The matrix elements of the second and third terms in Equation (5.3) are expressed in terms of a summation over the values of "n" and "ℓ" which represent occupied shells in the core of the element in question. In addition, the evaluation of the matrix elements of the Fock potential requires an integration over all of reciprocal space. We have been able to program the calculation of $\langle\underline{k}+\underline{q}|v_i|\underline{k}\rangle_{\Omega_o}$ such that the integration over reciprocal space, with a maximum error of one part in ten thousand, takes less than thirty seconds for each element for given values of $\underline{k}$ and $\underline{q}$. In Table 5.1, we have presented these matrix elements of the Hartree-Fock ionic potentials of lithium and magnesium in rydbergs for three values of $\underline{k}$ and several values of $\underline{q}$. These matrix elements depend upon the nature of the crystal only to the extent of a multiplicative factor of $1/\Omega_o$. We are considering a 50-50 alloy of lithium and magnesium in which the ionic sites form a body-centered cubic lattice with a cube edge of 3.5 Å. Accordingly,

Table 5.1

MATRIX ELEMENTS OF IONIC HARTREE-FOCK POTENTIALS

$\lvert \underline{k}' \rvert$	$\langle \underline{k} \lvert v_1 \rvert \underline{k}' \rangle$ for $\underline{k} = 0.0\ \hat{x}$	
	Lithium	Magnesium
0.25	-2.936161	-5.944271
0.5	-0.845845	-1.763288
1.0	-0.305571	-0.680483
1.5	-0.185479	-0.434633
2.0	-0.129164	-0.313642
2.5	-0.094584	-0.235121
3.0	-0.071176	-0.179453
4.0	-0.042772	-0.109171
5.0	-0.027501	-0.070728
6.0	-0.018740	-0.048906
7.0	-0.013411	-0.035877
8.0	-0.009995	-0.027644
9.0	-0.007704	-0.022136
10.0	-0.006104	-0.018250
11.0	-0.004950	-0.015379
12.0	-0.004092	-0.013175

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert v_i \rvert \underline{k}' \rangle$ for $\underline{k} = 0.5\ \hat{x}$ Lithium	Magnesium
0.75	0.0	0.250	-2.919494	-5.936771
0.50	0.25	0.250	-2.924553	-5.939447
0.25	0.0	0.250	-2.930145	-5.942026
1.0	0.0	0.500	-0.825925	-1.753819
0.5	0.5	0.500	-0.834976	-1.758822
0.0	0.0	0.500	-0.845849	-1.763288
1.5	0.0	1.000	-0.283729	-0.669665
0.911	0.911	1.000	-0.291015	-0.674109
-0.5	0.0	1.000	-0.314680	-0.681946
0.0	1.0	1.118	-0.264790	-0.598504
2.0	0.0	1.500	-0.166120	-0.426015
-1.0	0.0	1.500	-0.198268	-0.434738
0.0	1.5	1.581	-0.173081	-0.409453
2.5	0.0	2.000	-0.113922	-0.3087[illegible]
-1.5	0.0	2.000	-0.141422	-0.31106[illegible]
0.0	2.0	2.062	-0.123168	-0.301404
3.0	0.0	2.500	-0.083323	-0.233776
-2.0	0.0	2.500	-0.104503	-0.230132
0.0	2.5	2.550	-0.091045	-0.227995
3.5	0.0	3.000	-0.063110	-0.190736
-2.5	0.0	3.000	-0.078549	-0.172980
0.0	3.0	3.041	-0.068897	-0.175029
4.5	0.0	4.000	-0.038728	-0.112860
-3.5	0.0	4.000	-0.046461	-0.102233
0.0	4.0	4.031	-0.041701	-0.107387
5.5	0.0	5.000	-0.025425	-0.074537
-4.5	0.0	5.000	-0.029312	-0.065015
0.0	5.0	5.025	-0.026945	-0.070023
6.5	0.0	6.000	-0.017623	-0.052052
-5.5	0.0	6.000	-0.019656	-0.044693
0.0	6.0	6.021	-0.018423	-0.048656

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert v_i \rvert \underline{k}' \rangle$ for $\underline{k} = 1.0\,\hat{x}$ Lithium	Magnesium
1.25	0.0	0.250	-2.891948	-5.913778
1.00	0.25	0.250	-2.898507	-5.920518
0.75	0.0	0.250	-2.906145	-5.927444
1.5	0.0	0.500	-0.798769	-1.728808
1.0	0.5	0.500	-0.810358	-1.741082
0.5	0.0	0.500	-0.825925	-1.753819
2.0	0.0	1.000	-0.260159	-0.645446
1.0	1.0	1.000	-0.276797	-0.663013
0.0	0.0	1.000	-0.305571	-0.680483
0.0	1.0	1.414	-0.197519	-0.461632
2.5	0.0	1.500	-0.147593	-0.406580
1.435	1.435	1.500	-0.158350	-0.418001
-0.5	0.0	1.500	-0.198268	-0.434738
0.0	1.5	1.803	-0.145245	-0.351773
3.0	0.0	2.000	-0.100149	-0.295152
1.823	1.823	2.000	-0.107368	-0.302085
-1.0	0.0	2.000	-0.146166	-0.308819
0.0	2.0	2.236	-0.108296	-0.270265
3.5	0.0	2.500	-0.073369	-0.225361
-1.5	0.0	2.500	-0.110316	-0.225044
0.0	2.5	2.693	-0.081972	-0.209153
4.0	0.0	3.000	-0.055995	-0.176244
-2.0	0.0	3.000	-0.083627	-0.166052
0.0	3.0	3.162	-0.062975	-0.163117
5.0	0.0	4.000	-0.035073	-0.112721
-3.0	0.0	4.000	-0.049214	-0.094847
0.0	4.0	4.123	-0.038893	-0.102471
6.0	0.0	5.000	-0.023477	-0.075871
-4.0	0.0	5.000	-0.030609	-0.059164
0.0	5.0	5.099	-0.025481	-0.068027
7.0	0.0	6.000	-0.016532	-0.053626
-5.0	0.0	6.000	-0.020239	-0.040581
0.0	6.0	6.083	-0.017609	-0.047911

we set the ionic volume, Ω_o, equal to 144.671 (a.u.)^3. The values of $\underline{k}$ and $\underline{q}$ are given in atomic units and may be compared directly with the radius of the Fermi sphere, which is roughly 0.67 a.u. The maximum error in the matrix elements of the potentials is one part in ten thousand or $\pm$ 0.000001 rydbergs, whichever is the larger.

Matrix Elements of the Unscreened Pseudopotential

Referring to Equations (2.22) and (2.25), we may write the matrix elements of the unscreened pseudopotential for an individual ion as

$$\langle \underline{k} + \underline{q} | w_i^o | \underline{k} \rangle_{\Omega_o} = \langle \underline{k} + \underline{q} | v_i | \underline{k} \rangle_{\Omega_o} + N \Sigma_{n\ell ms} \langle \underline{k} + \underline{q} | n\ell ms; i \rangle \int d\underline{r}' f_{n\ell ms;i}(\underline{r}') \langle \underline{r}' | \underline{k} \rangle \ . \quad (5.27)$$

The sum extends over all the occupied core states associated with that ion. For the pseudopotential of Equation (5.1), we may write $f_{n\ell ms;i}(\underline{r}')$ as

$$f_{n\ell ms;i}(\underline{r}') = \langle n\ell ms; i | \underline{r}' \rangle (|\underline{k}|^2 + \bar{V}_L + \langle \underline{k} | W | \underline{k} \rangle - E_c) \ , \quad (5.28)$$

where $\langle \underline{k} | W | \underline{k} \rangle$ is given by Equation (5.2). Referring to that expression, we may note that $\langle \underline{k} | V^I | \underline{k} \rangle$ is just the average of the diagonal matrix elements of the Fock potentials of the two ions, weighted to account for their possibly different concentrations in the alloy. In our example, we have equal concentrations of the elements. Note that the spatial averages of the potential of the nucleii, the Hartree potential of the core electrons, and the Hartree potential

of the conduction electrons have been included in $\bar{V}_L$. Accordingly, the average of the first two contributions to v_i do not contribute to $\langle \underline{k}|W|\underline{k}\rangle$. Further, we have approximated V^{EL} in our formalism with a linearized Hartree potential, V^{sc}. This potential has no diagonal matrix elements between plane waves since the spatial average of this conduction electron potential has been included in $\bar{V}_L$. In order to evaluate the diagonal matrix elements of the screened pseudopotential, W, we need only the diagonal matrix elements of the Fock exchange potentials of the ions, the projections of the core states on the set of plane waves, and the values of the quantity $(\bar{V}_L - E_c)$. We have already calculated the first two quantities and need only evaluate $(\bar{V}_L - E_c)$. Since we have a direct expression for the diagonal matrix elements of W, we are only interested in the evaluation of the right-hand side of Equation (5.27) for $\underline{q} \neq 0$. This quantity depends upon $\langle \underline{k}|W|\underline{k}\rangle$, the off-diagonal matrix elements of v_i, the projections of the core states of the set of plane waves, and the values of $(\bar{V}_L - E_c)$. Therefore, we may readily evaluate the off-diagonal matrix elements of w_i^o once we have calculated the values of $(\bar{V}_L - E_c)$.

As we discussed in Chapter Two, we have restricted the form of $f_c(\underline{r}')$ which we might choose from our optimization procedure to one which is independent of the local environment of the ion with which it is associated, even though $f_c(\underline{r}')$ may vary as the ions are rearranged at constant volume. For the pseudopotential of Equation (5.1), this restriction constrains the value which we use for E_c to

being a function of only the type of ion with which it is associated and of the configuration of ions in the crystal. Since E_c is an eigenvalue of the crystalline Hamiltonian, H, we would expect that it would formally depend upon the local environment of the core state. However, we shall approximate E_c such that it is independent of local configuration. Thus, we are approximating the optimal pseudopotential which we discussed in Chapter Four.

In our assumption that the core eigenfunctions are essentially those of the corresponding atomic eigenstates, we have neglected the spatial variation over the core region of the crystalline potential less the atomic potential. While this approximation may be reasonable, we must account for the influence of the non-zero value of this correction potential at the site of the core on the eigenvalues of the core states. The atomic Hartree-Fock eigenvalues of the core states of lithium and magnesium as given by Clementi [1] are presented in rydbergs in Table 5.2. A precise calculation of the corrections to

Table 5.2

HARTREE-FOCK ATOMIC EIGENVALUES

Lithium		Magnesium	
1s	-2.47775	1s	-49.03165
		2s	-3.73048
		2p	-2.28219

these eigenvalues would begin by subtracting the influence of the valence states of the atom. Then we would add the influence of an

array of effective ionic potentials with a compensating uniform electronic charge distribution. This correction includes the effects of both the core charge and that charge which is orthogonalized out of the conduction electron gas by the operation of the pseudopotential. Finally, we would account for the influence of the screening distribution of conduction electrons. This final step would require a knowledge of the screening distribution and, hence, the use of a self-consistent procedure. In this instance, we may use an approximation to avoid such a procedure since any values for E_c will constitute a valid pseudopotential. Accordingly, we shall assume that the influence of the valence states on the core states approximates fairly well the influence of near conduction electrons. Acting on that assumption, we will not subtract the influence of the atomic valence states from the energies of the core electrons. After adding the influence of the array of effective ionic charges and the compensating uniform distribution of charges we shall subtract the interaction of the core charges with a sphere of this uniform charge density centered at the nucleus and containing the effective valence number of electrons. This procedure is probably at least as accurate as neglecting the influence of the screening in the procedure we described above, especially for an alloy. We should emphasize at this point that this procedure for determining the crystalline core eigenvalues yields a valid pseudopotential in the sense that the electron energies to all orders in

perturbation theory will be the actual crystalline energies. However, our approximation for the core eigenvalues makes the resulting pseudopotential an approximation to the optimal pseudopotential of Equation (5.1), and might accordingly lessen the accuracy of a second-order perturbation theory calculation of the energies.

We must first estimate the effective ionic charges. The core states associated with an ion of type i will interact with a plane wave $\underline{k}$ to add an amount of positive charge to the effective core charge equal to

$$\Sigma_{n\ell ms} \langle \underline{k} | n\ell ms;i \rangle \langle n\ell ms;i | \underline{k} \rangle \quad . \tag{5.29}$$

We have already evaluated the projection of the core states on the set of plane waves. In order to preserve charge neutrality, an equal amount of compensating negative charge is added to the charge density associated with the valence states of H_p. We will treat terms like Expression (5.29) as being related to a first-order expression in the pseudopotential, as we discussed in connection with the screening potential derivation in Chapter Two. We may then obtain a first order estimate of the total amount of positive charge added to the effective core charge by the interactions of the core states with all of the pseudovalence states by using a zero'th order approximation for the pseudovalence state associated with $\underline{k}$,

$$|\bar{v}\rangle \simeq a_o(\underline{k}) \; |\underline{k}\rangle \quad . \tag{5.30}$$

If Z_i is the core charge of an ion of type i, we may write the effective core charge, denoted by Z_i^{eff}, as

$$Z_i^{eff} = Z_i + \Sigma_{\{\underline{k}\}_F} |a_o(\underline{k})|^2 \, \Sigma_{n\ell ms} |\langle n\ell ms;i|\underline{k}\rangle|^2 \ , \tag{5.31}$$

where the sum in reciprocal space extends over all points within the Fermi sphere. As we demonstrate in our derivation of the screening potential, $|a_o(\underline{k})|^2$ depends upon a sum over all of the core states in the crystal and is given by

$$|a_c(\underline{k})|^2 = [1 - \Sigma_c \langle \underline{k}|c\rangle\langle c|\underline{k}\rangle]^{-1} \ . \tag{5.32}$$

If xN is the fraction of ions of type A in the alloy, we may use our previous discussion of the average and difference projection operators to write Expression (5.32) simply as

$$|a_o(\underline{k})|^2 = \left[1 - xN \, \Sigma_{n\ell ms} |\langle n\ell ms;A|\underline{k}\rangle|^2 - (1-x)N \, \Sigma_{n\ell ms} |\langle n\ell ms;B|\underline{k}\rangle|\right]^{-1} . \tag{5.33}$$

Thus we may evaluate each of the terms in the sum in Expression (5.31). If we now note that the density of electron states in reciprocal space is just $2\Omega/(2\pi)^3$, where the extra factor of two accounts for spin, we may write Equation (5.31) as

$$Z_i^{eff} = Z_i \frac{\Omega}{4\pi^3} \int_{\Omega_F} d\underline{k} |a_o(\underline{k})|^2 \, \Sigma_{n\ell ms} |\langle n\ell ms;i|\underline{k}\rangle|^2 \ . \tag{5.34}$$

We may now evaluate this expression readily. For the 50-50 alloy of lithium and magnesium which we discussed before, we have used Equation (5.34) to calculate the following: $Z_{Li}^{eff} = 1.11657$ and $Z_{Mg}^{eff} = 2.14834$. These effective ionic charges lead to an average

effective conduction electron density of 0.011284 electrons per $(a.u.)^3$.

Let us now calculate the potential at the core due to the array of effective ionic charges with a compensating uniform charge density. For the completely disordered crystal, we will consider an array of average charges, $\bar{Z}^{eff} = (Z_A^{eff} + Z_B^{eff})/2$, located on the set of body-centered cubic sites. We will consider them to be point charges in a uniform compensating distribution of electrons. The energy per ion for such a system has been found [3] to be

$$-1.79186 \frac{(\bar{Z}^{eff})^2}{r_o} , \tag{5.35}$$

in rydbergs, where r_o is the radius of a sphere of volume Ω_o. The effect of the potential $\bar{V}_L$ is to add an amount $\bar{V}_L$ to the value of E_c. Since E_c occurs in our pseudopotential only in the form $(\bar{V}_L - E_c)$, we may just set $\bar{V}_L$ equal to zero for the purpose of this calculation. Since we are considering only the Hartree potential of the ions and the uniform compensating electron density in this calculation, $\bar{V}_L$ is just the spatial average of the crystalline potential. If the average potential is zero, the uniform electron charge distribution will not contribute to the energy of the crystal. Therefore, the value of the potential at a site due to all the other ions in the crystal and the uniform compensating charge density must be

$$-2(1.79186)\,\frac{\bar{Z}^{eff}}{r_o}\ . \tag{5.36}$$

The core states will also see a potential due to the uniform charge density which goes as $|\underline{r}|^2$. Therefore, we may write the potential in the core region of an ion in the disordered crystal as

$$V^{i}_{DIS}(\underline{r}) = -2(1.79186)\,\frac{\bar{Z}^{eff}}{r_o} + \frac{4\pi}{3}\,\frac{\bar{Z}^{eff}}{\Omega_o}\,|\underline{r}|^2\ . \tag{5.37}$$

For the ordered crystal, we must add to Equation (5.37) the influence of an array of difference charges, $\pm\,\Delta Z^{eff} = \pm(Z_A^{eff} - Z_B^{eff})/2$, distributed on a cesium chloride lattice. The energy of such a system has been shown [4] to be

$$-1.002153\,\frac{(\Delta Z^{eff})^2}{r_o}\ , \tag{5.38}$$

in rydbergs, where r_o is the radius of a sphere of volume, Ω_o. There is no energy of interaction between these arrays. At a site containing an A ion, Expression (5.38) contributes a potential in the core region of

$$-2(1.002153)\,\frac{\Delta Z^{eff}}{r_o}\ . \tag{5.39}$$

This potential changes sign at a site containing a B ion. If we add this potential to that for the disordered crystal, we obtain the following expression for the potential at a site in the ordered alloy containing an A ion:

$$V^{A}_{ORD}(\underline{r}) = -\frac{1}{r_o}\,\{2.79401\,Z_A^{eff} + 0.78971\,Z_B^{eff}\} + \frac{2\pi}{3\Omega_o}\,(Z_A^{eff} + Z_B^{eff})\,|\underline{r}|^2\ . \tag{5.40}$$

In order to obtain the potential at a site containing a B ion, we need only interchange A and B wherever they occur in Expression (5.40). The correction to the energy of a core state due to these potentials is now given by

$$\Delta E^{1}_{n\ell ms;i} = \int d\underline{r}\ \langle n\ell ms;i|\underline{r}\rangle\ V^{i}_{\left\{\substack{ORD\\DIS}\right\}}(\underline{r})\langle \underline{r}|n\ell ms;i\rangle \quad . \tag{5.41}$$

The spatially varying parts of Equations (5.37) and (5.40) may be readily evaluated in terms of the expectation value of $|\underline{r}|^2$ in the core state. Thus we have obtained the first correction to the core eigenvalues.

Now we wish to evaluate the energy of interaction of a sphere of the uniform compensating charge density with a core charge. The radius of the sphere is determined by the requirement that it contain the effective number of valence electrons associated with the ion in question. This radius for an ion of type i, R^i_s, is given by

$$R^i_s = \left\{\frac{3Z_i^{eff}\ \Omega_o}{4\pi\ \bar{Z}^{eff}}\right\}^{\frac{1}{3}} \quad . \tag{5.42}$$

If we use the formula for the interaction energy between two charge distributions,

$$2\int d\underline{r}\int d\underline{r}'\ \frac{n_1(\underline{r})\ n_2(\underline{r}')}{|\underline{r}-\underline{r}'|} \quad , \tag{5.43}$$

we may write the interaction between the core state and the sphere of charge as

$$\Delta E^2_{n\ell ms;i} = 2 \int d\underline{r} |\langle n\ell ms;i|\underline{r}\rangle|^2 \int_0^{R_s^i} d|\underline{r}'| \; |\underline{r}'|^2 \frac{\bar{Z}^{eff}}{\Omega_o} \int d\Omega_{\underline{r}'} \frac{1}{|\underline{r}-\underline{r}'|} \; . \tag{5.44}$$

We may further expand the last factor in Equation (5.44) using Equation (5.19) and perform the angular integrations associated with $\underline{r}'$ to obtain

$$\Delta E^2_{n\ell ms;i} = \frac{8\pi \bar{Z}^{eff}}{\Omega_o} \int d\underline{r} \; |\langle n\ell ms;i|\underline{r}\rangle|^2 \int_0^{R_s^i} d|\underline{r}'| \; \frac{|\underline{r}'|^2}{|r_>|} \; . \tag{5.45}$$

We may insert the form of the Clementi core wavefunctions into Equation (4.45) and perform the angular integration readily. We may then evaluate the second correction to the energy of the core state once we perform integrals like

$$I_1(n,a) = \int_0^{R_s^i} dx \; x^n \; e^{-ax} \qquad \text{for} \quad n = 2,3,\ldots \tag{5.46}$$

and

$$I_2(n,a) = \int_{R_s^i}^{\infty} dx \; x^n \; e^{-ax} \qquad \text{for} \quad n = 1,2,3,\ldots \; . \tag{5.47}$$

In connection with the evaluation of these integrals, we may note immediately that

$$I_1(n,a) + I_2(n,a) = \frac{n!}{a^{n+1}} \; , \tag{5.48}$$

and that

$$I_1(1,a) = \frac{1}{a^2} \{1 - e^{-aR_s^i}(aR_s^i + 1)\} \; . \tag{5.49}$$

We may integrate $I_1(n,a)$ by parts to obtain

$$I_1(n,a) = \frac{n}{a} I_1(n-1,a) - \frac{(R_s^i)^n \; e^{-aR_s^i}}{a} \; . \tag{5.50}$$

Thus we are in a position to evaluate all the integrals given by Equations (5.46) and (5.47), and thereby obtain the second correction to the eigenvalues of the core states.

We have calculated the total correction to the core eigenvalues suggested by Equations (5.41) and (5.45) for the alloy of lithium and magnesium which we are considering. These corrections are listed in rydbergs in Table 5.3. The values in this table should be added to the appropriate values in Table 5.2 to obtain values of $(E_c - \bar{V}_L)$.

Table 5.3

CRYSTALLINE CORE ENERGY CORRECTIONS

I. Ordered Crystal				II. Disordered Crystal			
Lithium		Magnesium		Lithium		Magnesium	
1s	+0.31148	1s	+0.03724	1s	+0.62898	1s	-0.00951
		2s	+0.03720			2s	-0.00955
		2p	+0.03723			2p	-0.00952

The corrections which we found for magnesium are small due to the close cancellation of the two different energy corrections.

We are now in a position to calculate the off-diagonal matrix elements of the unscreened pseudopotential and the diagonal matrix elements of the screened pseudopotential. We shall calculate both of these quantities for three different sets of eigenvalues: atomic; ordered crystalline; and disordered crystalline. In this manner, we

may determine the influence upon our final results of the choice of core eigenvalues. We will also be able to estimate the sensitivity of our results to the approximations involved in our procedure for estimating the crystalline core eigenvalues. The diagonal matrix elements of the screened pseudopotential as defined by Equation (5.2) have been tabulated in rydbergs in Table 5.4. These matrix elements have been evaluated for three values of $\underline{k}$ in atomic units and the three sets of core eigenvalues as shown. We have used these matrix

Table 5.4

DIAGONAL MATRIX ELEMENTS OF
THE SCREENED PSEUDOPOTENTIAL

$\lvert\underline{k}\rvert$	$\langle\underline{k}\lvert W\rvert\underline{k}\rangle$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.0	0.115084	0.098642	0.086029
0.5	0.119322	0.105251	0.095103
1.0	0.130186	0.120762	0.115050

elements to calculate the off-diagonal matrix elements of the unscreened pseudopotential as given by Equation (5.27). We then found the unscreened average and difference pseudopotentials for our 50-50 of lithium and magnesium as defined in Equations (2.27) and (2.28). These potentials are tabulated in rydbergs in Tables 5.5 and 5.6. As in the case of the matrix elements of the ionic potentials, the

Table 5.5

MATRIX ELEMENTS OF UNSCREENED AVERAGE PSEUDOPOTENTIALS

$\lvert \underline{k}' \rvert$	$\langle \underline{k} \lvert \bar{w}^{\circ} \rvert \underline{k}' \rangle$ for $\underline{\kappa} = 0.0\,\hat{x}$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.25	-4.139430	-4.155507	-4.167834
0.5	-1.019360	-1.034472	-1.046027
1.0	-0.256443	-0.268602	-0.277821
1.5	-0.130289	-0.139183	-0.145894
2.0	-0.091363	-0.097532	-0.102201
2.5	-0.072556	-0.076740	-0.079952
3.0	-0.059659	-0.062486	-0.064717
4.0	-0.040637	-0.041963	-0.043103
5.0	-0.027628	-0.028285	-0.028920
6.0	-0.019117	-0.019462	-0.019842
7.0	-0.013663	-0.013855	-0.014095
8.0	-0.010161	-0.010272	-0.010432
9.0	-0.007876	-0.007943	-0.008053
10.0	-0.006348	-0.006390	-0.006468
11.0	-0.005294	-0.005321	-0.005378
12.0	-0.004540	-0.004558	-0.004600

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert \bar{w}^{\circ} \rvert \underline{k}' \rangle$ for $\underline{k} = 0.5\,\hat{x}$		
			Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.75	0.0	0.250	-4.141143	-4.154103	-4.163187
0.50	0.25	0.250	-4.132298	-4.140138	-4.156052
0.25	0.0	0.250	-4.126459	-4.141241	-4.152202
1.0	0.0	0.500	-1.025602	1.037188	-1.045089
0.5	0.5	0.500	-1.006657	1.019830	-1.029108
0.0	0.0	0.500	-0.998821	-1.013741	-1.025098
1.5	0.0	1.000	-0.267662	-0.276311	-0.281935
0.911	0.911	1.000	-0.249625	-0.259499	-0.266042
-0.5	0.0	1.000	-0.195654	-0.209725	-0.219873
0.0	1.0	1.118	-0.167377	-0.178962	-0.186864
2.0	0.0	1.500	-0.139918	-0.146029	-0.149863
-1.0	0.0	1.500	-0.052232	-0.063818	-0.071720
0.0	1.5	1.581	-0.082232	-0.090881	-0.096505
2.5	0.0	2.000	-0.097578	-0.101796	-0.104388
-1.5	0.0	2.000	-0.017207	-0.025856	-0.031480
0.0	2.0	2.062	-0.056137	-0.062248	-0.066082
3.0	0.0	2.500	-0.075933	-0.078831	-0.080606
-2.0	0.0	2.500	-0.011168	-0.017280	-0.021114
0.0	2.5	2.550	-0.045762	-0.049980	-0.052572
3.5	0.0	3.000	-0.061220	-0.063224	-0.064466
-2.5	0.0	3.000	-0.012007	-0.016225	-0.018817
0.0	3.0	3.041	-0.039347	-0.042245	-0.044019
4.5	0.0	4.000	-0.040768	-0.041765	-0.042419
-3.5	0.0	4.000	-0.013644	-0.015648	-0.016890
0.0	4.0	4.031	-0.029009	-0.030412	-0.031303
5.5	0.0	5.000	-0.027590	-0.028115	-0.028493
-4.5	0.0	5.000	-0.012138	-0.013134	-0.013789
0.0	5.0	5.025	-0.020828	-0.021546	-0.022038
6.5	0.0	6.000	-0.019183	-0.019475	-0.019708
-5.5	0.0	6.000	-0.009784	-0.010309	-0.010688
0.0	6.0	6.021	-0.015002	-0.015391	-0.015686

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert \bar{w}^{\circ} \rvert \underline{k}' \rangle$ for $\underline{k} = 1.0\,\hat{x}$		
			Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
1.25	0.0	0.250	-4.137472	-4.145754	-4.150533
1.00	0.25	0.250	-4.121758	-4.131045	-4.136639
0.75	0.0	0.250	-4.107433	-4.117890	-4.124567
1.5	0.0	0.500	-1.026612	-1.033751	-1.037687
1.0	0.5	0.500	-0.996449	-1.005341	-1.010604
0.5	0.0	0.500	-0.971214	-0.982468	-0.990052
2.0	0.0	1.000	-0.271377	-0.276488	-0.279089
1.0	1.0	1.000	-0.222891	-0.230417	-0.234630
0.0	0.0	1.000	-0.189702	-0.201400	-0.210165
0 0	1.0	1.414	-0.038994	-0.048419	-0.054131
2.5	0.0	1.500	-0.142440	-0.146009	-0.147720
1.435	1.435	1.500	-0.109862	-0.114866	-0.117402
-0.5	0.0	1.500	0.002156	-0.009097	-0.016682
0.0	1.5	1.803	-0.011333	-0.018472	-0.022407
3.0	0.0	2.000	-0.098445	-0.100926	-0.102071
1.823	1.823	2.000	-0.076338	-0.079711	-0.081316
-1.0	0.0	2.000	0.063089	0.053665	0.047952
0.0	2.0	2.236	-0.007855	-0.012965	-0.015567
3.5	0.0	2.500	-0.075707	-0.077442	-0.078230
-1.5	0.0	2.500	0.069497	0.062358	0.058422
0.0	2.5	2.693	-0.010916	-0.014486	-0.016197
4.0	0.0	3.000	-0.060513	-0.061741	-0.062300
-2.0	0.0	3.000	0.056586	0.051475	0.048874
0.0	3.0	3.162	-0.013840	-0.016321	-0.017466
5.0	0.0	4.000	-0.040095	-0.040736	-0.041042
-3.0	0.0	4.000	0.027175	0.024694	0.023549
0.0	4.0	4.123	-0.015076	-0.016304	-0.016862
6.0	0.0	5.000	-0.027281	-0.02[illegible]36	-0.027819
-4.0	0.0	5.000	0.010720	0.009492	0.008933
0.0	5.0	5.099	-0.012952	-0.013594	-0.013899
7.0	0.0	6.000	-0.019158	-0.019365	-0.019482
-5.0	0.0	6.000	0.003383	0.002741	0.002436
0.0	6.0	6.083	-0.010367	-0.010722	-0.010905

Table 5.6

MATRIX ELEMENTS OF UNSCREENED DIFFERENCE PSEUDOPOTENTIALS

$\lvert \underline{k}' \rvert$	$\langle \underline{k} \lvert \Delta w^{\circ} \rvert \underline{k}' \rangle$ for $\underline{k} = 0.0\,\hat{x}$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.25	1.420381	1.409000	1.393684
0.5	0.377289	0.366628	0.352240
1.0	0.114076	0.105594	0.094035
1.5	0.063874	0.057710	0.049262
2.0	0.044917	0.040624	0.034762
2.5	0.034514	0.031546	0.027560
3.0	0.027267	0.025189	0.022482
4.0	0.016963	0.015873	0.014582
5.0	0.010265	0.009640	0.008985
6.0	0.006150	0.005766	0.005411
7.0	0.003742	0.003492	0.003288
8.0	0.002382	0.002213	0.002090
9.0	0.001640	0.001522	0.001445
10.0	0.001251	0.001165	0.001115
11.0	0.001058	0.000993	0.000959
12.0	0.000965	0.000918	0.000894

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert \Delta w^\circ \rvert \underline{k}' \rangle$ for $\underline{k} = 0.5\,\hat{x}$		
			Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.75	0.0	0.250	1.408066	1.399710	1.387340
0.50	0.25	0.250	1.408996	1.399824	1.386577
0.25	0.0	0.250	1.415052	1.404822	1.390611
1.0	0.0	0.500	0.364102	0.356886	0.345867
0.5	0.5	0.500	0.361627	0.353081	0.340500
0.0	0.0	0.500	0.376729	0.366064	0.351669
1.5	0.0	1.000	0.103888	0.098821	0.090640
0.911	0.911	1.000	0.096791	0.090864	0.081504
-0.5	0.0	1.000	0.086276	0.076872	0.063393
0.0	1.0	1.118	0.067012	0.059796	0.048776
2.0	0.0	1.500	0.057135	0.053717	0.047961
-1.0	0.0	1.500	0.018390	0.011174	0.000154
0.0	1.5	1.581	0.029106	0.024039	0.015858
2.5	0.0	2.000	0.040622	0.038326	0.034362
-1.5	0.0	2.000	-0.004260	-0.009327	-0.017508
0.0	2.0	2.062	0.016306	0.012888	0.007132
3.0	0.0	2.500	0.031685	0.030115	0.027393
-2.0	0.0	2.500	-0.009998	-0.013416	-0.019172
0.0	2.5	2.550	0.011682	0.009386	0.005422
3.5	0.0	3.000	0.025283	0.024180	0.022295
-2.5	0.0	3.000	-0.009578	-0.011874	-0.015837
0.0	3.0	3.041	0.009525	0.007955	0.005232
4.5	0.0	4.000	0.015928	0.015337	0.014393
-3.5	0.0	4.000	-0.005644	-0.006747	-0.008632
0.0	4.0	4.031	0.006549	0.005752	0.004428
5.5	0.0	5.000	0.009810	0.009462	0.008959
-4.5	0.0	5.000	-0.003286	-0.003878	-0.004821
0.0	5.0	5.025	0.004097	0.003647	0.002964
6.5	0.0	6.000	0.006052	0.005830	0.005546
-5.5	0.0	6.000	-0.002226	-0.002576	-0.003078
0.0	6.0	6.[illegible]1	0.002390	0.002114	0.001739

k'_x	k'_y	$\lvert \underline{k} - \underline{k}' \rvert$	$\langle \underline{k} \lvert \Delta w^\circ \rvert \underline{k}' \rangle$ for $\underline{k} = 1.0\ \hat{x}$		
			Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
1.25	0.0	0.250	1.389307	1.384801	1.376699
1.00	0.25	0.250	1.387285	1.381983	1.372882
0.75	0.0	0.250	1.390488	1.384117	1.373845
1.5	0.0	0.500	0.349589	0.345900	0.338929
1.0	0.5	0.500	0.342035	0.337056	0.328349
0.5	0.0	0.500	0.353655	0.346376	0.335295
2.0	0.0	1.000	0.095799	0.093386	0.088411
1.0	1.0	1.000	0.075200	0.071243	0.063890
0.0	0.0	1.000	0.111230	0.102728	0.091150
0.0	1.0	1.414	0.008355	0.002936	-0.006301
2.5	0.0	1.500	0.052662	0.051090	0.047621
1.435	1.435	1.500	0.034202	0.031851	0.026980
-0.5	0.0	1.500	0.007944	0.000664	-0.010417
0.0	1.5	1.803	-0.012167	-0.015856	-0.022827
3.0	0.0	2.000	0.037954	0.036908	0.034500
1.823	1.823	2.000	0.023454	0.021981	0.018705
-1.0	0.0	2.000	-0.042375	-0.047794	-0.057031
0.0	2.0	2.236	-0.015861	-0.018273	-0.023249
3.5	0.0	2.500	0.029916	0.029199	0.027516
-1.5	0.0	2.500	-0.058067	-0.061756	-0.068727
0.0	2.5	2.693	-0.013241	-0.014813	-0.018282
4.0	0.0	3.000	0.024046	0.023537	0.022346
-2.0	0.0	3.000	-0.055632	-0.058044	-0.063020
0.0	3.0	3.162	-0.009477	-0.010523	-0.012931
5.0	0.0	4.000	0.015389	0.015108	0.014485
-3.0	0.0	4.000	-0.036732	-0.037778	-0.040186
0.0	4.0	4.123	-0.004289	-0.004799	-0.005989
6.0	0.0	5.000	0.009708	0.009538	0.009192
-4.0	0.0	5.000	-0.021801	-0.022310	-0.023501
0.0	5.0	5.099	-0.002163	-0.002443	-0.003066
7.0	0.0	6.000	0.006195	0.006084	0.005882
-5.0	0.0	6.000	-0.013275	-0.013555	-0.014178
0.0	6.0	6.083	-0.001338	-0.001508	-0.001854

maximum error in these figures is one part in ten thousand or 0.000001 rydbergs, whichever is the greater.

Matrix Elements of the Screening Potential

Let us turn now to the matrix elements of the average and difference screening potentials as defined in Equations (2.69) and (2.70). Since we are seeking a first-order expression for the pseudopotential, we may replace the sum over the states contained in the Fermi volume with an integral over the free-electron Fermi sphere. We must remember a factor of two to account for the spins of the plane waves. The matrix elements of the unscreened pseudopotential obtained from Clementi's wavefunctions are real, and are intrinsically Hermitian due to the form of the pseudopotential which we selected. Further, these matrix elements depend only upon the magnitudes of the two plane waves and the angle between them. Accordingly, we may rewrite the formula for the average screening potential to obtain

$$\langle \underline{q}|\bar{v}^{sc}|0\rangle = \frac{2}{\pi^2|\underline{q}|^2 D(\underline{q})} \int_{\Omega_F} d\underline{k}\,|a_o(\underline{k})|^2 \left\{ \frac{2\langle \underline{k}+\underline{q}|\bar{w}^o|\underline{k}\rangle}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} + \bar{b}(\underline{k},\underline{q}) \right\} , \qquad (5.51)$$

where

$$D(\underline{q}) = 1 - \frac{4}{\pi^2|\underline{q}|^2} \int_{\Omega_F} d\underline{k}\, \frac{|a_o(\underline{k})|^2}{|\underline{k}|^2-|\underline{k}+\underline{q}|^2} \quad . \qquad (5.52)$$

The difference screening potential is given by an analogous expression. We have already discussed the evaluation of all components

in these integrands except $\bar{b}(\underline{k},\underline{q})$ and $\Delta b(\underline{k},\underline{q})$. In Chapter Two, we defined these in terms of an ionic quantity, $b_i(\underline{k},\underline{q})$, using Equations (2.65) and (2.66). We may write this ionic quantity as

$$b_i(\underline{k},\underline{q}) = -N \sum_{n\ell ms} \{ \langle \underline{k}+\underline{q} | n\ell ms;i \rangle \langle n\ell ms;i | \underline{k} \rangle + \langle \underline{k} | n\ell ms;i \rangle \langle n\ell ms;i | \underline{k}-\underline{q} \rangle \}$$
$$+N \sum_{\substack{n\ell ms \\ n'\ell'm's'}} \langle \underline{k} | n\ell ms;i \rangle \int d\underline{r} \langle n\ell ms;i | \underline{r} \rangle \, e^{-i\underline{q}\cdot\underline{r}} \langle \underline{r} | n'\ell'm's';i \rangle \times \langle n'\ell'm's'; | \underline{k} \rangle \quad . \tag{5.53}$$

Aside from the projections of core states on the set of plane waves, which we have already discussed, we need only evaluate the matrix elements of $\exp(-i\underline{q}\cdot\underline{r})$ between two core states on the same ion. We may simplify the evaluation of this factor by considering the integral of the product of Expression (5.53) and $|a_o(\underline{k})|^2$ over the Fermi sphere. This is the form in which Expression (5.53) will contribute to the screening. We may insert the form of the projection of the core states on plane waves given by Equation (5.23) into this integral and perform the angular integration to obtain

$$\frac{(4\pi)^2}{\Omega_o} \int_0^{k_F} d|\underline{k}| \; |\underline{k}|^2 |a_o(\underline{k})|^2 \sum_{\substack{n\ell m \\ n'}} \int_0^\infty d|\underline{r}| \; |\underline{r}|^2 j_\ell(|\underline{k}||\underline{r}|) \, R_{n\ell}(|\underline{r}|)$$
$$\times \int_0^\infty d|\underline{r}'| \; |\underline{r}'|^2 j_\ell(|\underline{k}||\underline{r}'|) \, R_{n'\ell}(|\underline{r}'|)$$
$$\times \int d\underline{r}'' \; e^{-i\underline{q}\cdot\underline{r}''} \langle n\ell ms;i | \underline{r}'' \rangle \langle \underline{r}'' | n'\ell ms;i \rangle \quad . \tag{5.54}$$

We have used the spherical symmetry of $|a_o(\underline{k})|^2$ and the orthonormality of the set of spherical harmonics to achieve this form. We may now

perform the summation over "m" and use Equation (5.13) to demonstrate the spherical symmetry of the core state contribution to the last integral over real space. Accordingly, if we expand the plane wave using Equation (5.14), the angular integration over real space singles out that component of the plane wave with l = 0. Therefore, we may write Expression (5.54) as

$$\frac{(4\pi)^2}{\Omega_o} \int_0^{k_F} d|\underline{k}|\ |\underline{k}|^2 |a_o(\underline{k})|^2 \Sigma_{nn',\ell}(2\ell+1) \int_0^\infty d|\underline{r}|\ |\underline{r}|^2 j_\ell(|\underline{k}||\underline{r}|) R_{n\ell}(|\underline{r}|)$$
$$\times \int^\infty d|\underline{r}'|\,|\underline{r}'|^2 j_\ell(|\underline{k}||\underline{r}'|) R_{n',\ell}(|\underline{r}'|)$$
$$\times \int_0^\infty d|\underline{r}''|\ |\underline{r}''|^2 j_o(|\underline{q}|\ |\underline{r}''|)\ R_{n\ell}(|\underline{r}''|)\ R_{n',\ell}(|\underline{r}''|) \quad . \tag{5.55}$$

We have already discussed the evaluation of this last integral in connection with the matrix elements of the second term in v_i. We have now established a procedure for the evaluation of the integrals of $\bar{b}(\underline{k},\underline{q})$ and $\Delta b(\underline{k},\underline{q})$ over the Fermi sphere. Hence, we can calculate the screening potential matrix elements once we have a procedure for performing the integral of the first term in the integrand over the Fermi sphere.

For values of $|\underline{q}|$ larger than twice the radius of the Fermi sphere, the denominator in the integrands of Equations (5.51) and (5.52) does not vanish for any points $\underline{k}$ in the Fermi sphere. In these instances, the integration may be performed directly using a computer. For values of $|\underline{q}|$ less than twice the radius of the Fermi sphere, we may note that the denominator in these integrands vanishes

for values of $\underline{k}$ lying on a plane which intersects the Fermi sphere. The evaluation of this integral is similar to the evaluation of

$$\int_{-a}^{b} \frac{f(x)}{x}\, dx \quad , \tag{5.56}$$

where f(x) is a slowly varying function in the immediate vicinity of x = 0, and a and b are both positive. The analytic procedure of finding the principal part is equivalent to replacing x in the denominator by $(x + i\epsilon)$ and finding the limit of the integral as ϵ approaches zero. In a computer calculation, we may let 1/x become

$$\frac{x}{x^2 + \delta} \quad , \tag{5.57}$$

and then calculate Expression (5.56) for several values of δ approaching zero. We found that this procedure converged quite slowly toward the limiting value and that the selection of small values of δ greatly increased the computation time. The slow convergence of the procedure is most likely due to the difference between 1/x and Expression (5.57) at the boundaries of the integral. Accordingly, we let 1/x become

$$\frac{x}{x^2 + \delta \exp(-x^2/\delta)} \quad . \tag{5.58}$$

This expression approaches 1/x much more rapidly than Expression (5.57) as x deviates from x = 0. But, the variation of Expression (5.58) as a function of x is not much more rapid than the variation of Expression (5.57). Therefore, we were able to achieve far greater accuracy using the latter form with little increase in computation time. This procedure is suitable for calculating the matrix elements of the screening

potential for small values of $|\underline{q}|$ to within one part in one or two hundred of the screened pseudopotential. For small values of $|\underline{q}|$, this often means a maximum error of one part in one thousand of the screening potential.

We have calculated the matrix elements of the average and difference screening potentials for the 50-50 alloy of lithium and magnesium using the above procedure. We have tabulated the values of these matrix elements in rydbergs for the three sets of core energies in Tables 5.7 and 5.8. The values of $|\underline{q}|$ are given in atomic units. The maximum error in the matrix elements is 0.1% for $|\underline{q}| = 0.25$, 0.3% for $|\underline{q}| = 0.50$, and 1.0% for $|\underline{q}| = 1.00$. For the other values of $|\underline{q}|$, there is no singularity in the screening integration. The maximum error in these matrix elements is one part per hundred or 0.000001 rydbergs, whichever is the greater.

We now have all the information which we need to calculate the off-diagonal matrix elements of the screened pseudopotential. We have not tabulated these results due to the much greater accuracy of the matrix elements of the unscreened pseudopotential relative to those of the matrix elements of the screening potential. We have already displayed the behavior of certain matrix elements of the screened pseudopotential in Figures 4.1 through 4.6. Both the pseudopotential denoted by "Present P.P." and that denoted by "Harrison P.P." were calculated according to the previous discussion in this chapter. The pseudopotential which we have chosen to use, denoted by "Present P.P.",

Table 5.7

MATRIX ELEMENTS OF AVERAGE SCREENING POTENTIAL

$\lvert \underline{q} \rvert$	$\langle \underline{q} \lvert \bar{v}^{sc} \rvert 0 \rangle$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.25	3.846227	3.858054	3.866265
0.5	0.770964	0.780587	0.787352
1.0	0.090946	0.095662	0.099141
1.5	0.009699	0.010772	0.011583
2.0	0.001900	0.002124	0.002294
2.5	0.001120	0.001180	0.001227
3.0	0.000926	0.000945	0.000960
4.0	0.000664	0.000667	0.000669
5.0	0.000470	0.000470	0.000471
6.0	0.000339	0.000340	0.000340

Table 5.8

MATRIX ELEMENTS OF DIFFERENCE SCREENING POTENTIAL

$\lvert \underline{q} \rvert$	$\langle \underline{q} \lvert \Delta v^{sc} \rvert 0 \rangle$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.25	-1.296334	-1.288873	-1.277672
0.5	-0.273529	-0.267340	-0.258193
1.0	-0.039776	-0.036535	-0.032006
1.5	-0.003984	-0.003222	-0.002186
2.0	0.000533	0.000692	0.000908
2.5	0.000803	0.000847	0.000905
3.0	0.000663	0.000678	0.000696
4.0	0.000409	0.000412	0.000414
5.0	0.000273	0.000273	0.000274
6.0	0.000196	0.000196	0.000196

demonstrates a marked improvement over the actual crystalline potential, which is a sum of the contributions of the ionic potentials and the screening potential.

The Energy-Wavenumber Characteristics

As we demonstrated in Chapter Two, the energy-wavenumber characteristics are central quantities if we are interested in the changes in the total conduction electron energy when the ions in the solid are rearranged at constant ionic volume. The energy-wavenumber characteristics are defined by Equation (2.84). We have evaluated the matrix elements of the screened pseudopotential and of the screening potential which occur in this expression. The integral over the Fermi sphere may be evaluated using the procedure which we discussed in the screening potential integration. We may note that $E_{12}(\underline{q}) = E_{21}(\underline{q})$ since the pseudopotential which we have used is Hermitian and the matrix elements of the potentials involved are real. Therefore, we have three distinct energy-wavenumber characteristics, $E_{11}(\underline{q})$ with the average-average potentials, $E_{12}(\underline{q})$ with the average-difference potentials, and $E_{22}(\underline{q})$ with the difference-difference potentials. Each of these energy-wavenumber characteristics has been evaluated for each of the sets of core eigenvalues which we discussed before. These values are presented in rydbergs in Tables 5.9, 5.10, and 5.11. As we noted in the tables, we have actually tabulated the product of $|\underline{q}|^2$ and the appropriate energy-wavenumber characteristic associated with that value of $\underline{q}$, as

Table 5.9

ENERGY-WAVENUMBER CHARACTERISTIC:

AVERAGE-AVERAGE POTENTIAL

$\lvert \underline{q} \rvert$	$\lvert \underline{q} \rvert^2 E_{11}(\lvert \underline{q} \rvert)$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.0	-0.195439	-0.195439	-0.195439
0.25	-0.180312	-0.181419	-0.182193
0.5	-0.14433	-0.14784	-0.15035
1.0	-0.07093	-0.07743	-0.08241
1.5	-0.02467	-0.02820	-0.03103
2.0	-0.01179	-0.01344	-0.01476
2.5	-0.00749	-0.00837	-0.00908
3.0	-0.00520	-0.00569	-0.00609
4.0	-0.00269	-0.00283	-0.00298
5.0	-0.00150	-0.00155	-0.00160
6.0	-0.00097	-0.00097	-0.00101

Table 5.10

ENERGY-WAVENUMBER CHARACTERISTIC:

AVERAGE-DIFFERENCE POTENTIAL

$\lvert \underline{q} \rvert$	$\lvert \underline{q} \rvert^2 E_{12}(\lvert \underline{q} \rvert)$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.0	0.065146	0.065146	0.065146
0.25	0.061165	0.061000	0.060602
0.5	0.05165	0.05113	0.04987
1.0	0.03182	0.03098	0.02867
1.5	0.01327	0.01293	0.01172
2.0	0.00635	0.00619	0.00563
2.5	0.00380	0.00370	0.00340
3.0	0.00239	0.00232	0.00216
4.0	0.00088	0.00085	0.00080
5.0	0.00023	0.00020	0.00018
6.0	-0.00007	-0.00007	-0.00007

Table 5.11

ENERGY-WAVENUMBER CHARACTERISTIC:

DIFFERENCE-DIFFERENCE POTENTIAL

$\lvert \underline{q} \rvert$	$\lvert \underline{q} \rvert^2 E_{22}(\lvert \underline{q} \rvert)$		
	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
0.0	-0.021715	-0.021715	-0.021715
0.25	-0.020746	-0.020511	-0.020161
0.5	-0.01846	-0.01766	-0.01653
1.0	-0.01436	-0.01244	-0.01001
1.5	-0.00744	-0.00613	-0.00459
2.0	-0.00366	-0.00305	-0.00233
2.5	-0.00219	-0.00188	-0.00151
3.0	-0.00140	-0.00123	-0.00104
4.0	-0.00062	-0.00056	-0.00051
5.0	-0.00033	-0.00030	-0.00028
6.0	-0.00022	-0.00022	-0.00018

given in atomic units. Since we will be interested only in integrals or sums of these functions over reciprocal space, the factor of $|\underline{q}|^2$ has been added to account for the large number of points associated with a given magnitude of $\underline{q}$ for large $|\underline{q}|$. The values of the energy-wavenumber characteristics for $\underline{q} = 0.0$ were obtained through a limiting procedure suggested by Harrison [5].

The Ordering Energy and the Effective Pairwise Interaction

Referring to Chapter Two, we note that Expression (2.86) gives that part of the total conduction electron energy which might vary as the ions are rearranged at constant volume. We are now in a position to evaluate this expression. Harrison [6] has demonstrated that the influence on the total energy of the sum of the diagonal matrix elements of W over the Fermi volume can be represented in this context to second order in the pseudopotential by performing an integration over the Fermi sphere. We may evaluate this term using the values given in Table 5.4. From our discussion of $F(\underline{q})$ in Chapter Three, we observe that $|F(\underline{q})|^2$ is equal to $1/N$ in the completely disordered crystal, except in that it vanishes for those values of $\underline{q}$ which are members of $\{\underline{K}\}$. In the completely ordered state of the alloy which we are discussing, $|F(\underline{q})|^2$ is unity for all $\underline{q}$ which belong to $\{\underline{K}_a\}$ and is zero elsewhere. Recall that the set $\{\underline{K}_a\}$ consists of all those reciprocal lattice vectors associated with the superlattice which have not already been included in $\{\underline{K}\}$.

We may now evaluate the remainder of Expression (2.86) for the states of complete order and complete disorder. In the ordered state, we merely sum $E_{11}(\underline{q})$ over all members of $\{\underline{K}\}$ and $E_{22}(\underline{q})$ over all members of $\{\underline{K}_a\}$. In the completely disordered state, we sum over the values of $E_{11}(\underline{q})$ as in the ordered state, but the contribution from $E_{22}(\underline{q})$ becomes

$$\frac{\Omega_o}{(2\pi)^3} \int d\underline{q}\, E_{22}(\underline{q}) \quad . \tag{5.59}$$

We have evaluated these contributions to Expression (2.86) for each set of core energies and placed the results in rydbergs in Table 5.12. Under these contributions, we have placed the total values of Expression (2.86) for the ordered and for the disordered states, calculated using each set of core energies.

The pseudopotentials calculated using these three sets of core energies are essentially three different pseudopotentials. However, each of these three pseudopotentials is in the Austin, Heine, and Sham form, and accordingly should yield the exact electronic eigenvalues if all orders in perturbation theory are included in the calculation. Therefore, we would expect that the total energies in Table 5.12 would be identical from column to column if second order perturbation theory, as we have applied it, suffices to determine these energies exactly. The differences between these values for Expression (2.86) is at least three times the differences which might have been introduced by our numerical procedures. The discrepancy between the results of these different

Table 5.12

STRUCTURE-DEPENDENT CONDUCTION ELECTRON ENERGY

	Atomic Core Energies	Ordered Crystalline Core Energies	Disordered Crystalline Core Energies
$\frac{1}{N}\Sigma_{\{\underline{k}\}_F}\langle\underline{k}\|\bar{w}\|\underline{k}\rangle$	0.179493	0.158613	0.143611
$\Sigma'_{\{\underline{q}\}}\delta_{\underline{q},\{\underline{K}\}}E_{11}(\underline{q})$	-0.363915	-0.405407	-0.438789
$\Sigma'_{\{\underline{q}\}}\delta_{\underline{q},\{\underline{K}_a\}}E_{22}(\underline{q})$	-0.150621	-0.130291	-0.105480
$\frac{\Omega_o}{(2\pi)^3}\int d\underline{q}\ E_{22}(\underline{q})$	-0.223425	-0.204080	-0.180210
Total for Ordered Crystal	-0.335043	-0.377085	-0.400658
Total for Disordered Crystal	-0.407847	-0.450874	-0.475388
Conduction Electron Contribution to the Ordering Energy	0.072 804	0.073789	0.074730

pseudopotentials is then a measure of our inability to evaluate the total conduction electron energy in our system using second order perturbation theory. Our best estimates of the core eigenvalues for this system should be either the ordered crystalline or the disordered crystalline core energies. Therefore, the minimum possible error in our evaluation of Expression (2.86) using one or the other of these sets is $\pm$ 0.013 rydbergs. We should emphasize that this is a minimum error.

If we now subtract the disordered total energy from the ordered total energy in each column, we obtain an estimate from each pseudopotential of the total conduction electron contribution to the ordering energy. These estimates appear in the last row of Table 5.12. The difference in these values is no larger than the difference which might have been introduced by our numerical procedures. We are led to expect that the values obtained from either the ordered crystalline or the disordered crystalline core energies would have a minimum error of $\pm$ 0.0005 rydbergs. The actual error introduced by our numerical procedures could be as large as $\pm$ 0.001 rydbergs. In any case, the minimum error which we might expect in our estimate of the conduction electron contribution to the ordering energy is much smaller than that in our estimate of the total conduction electron energy. The total conduction electron contribution to the ordering energy is represented by the difference between a sum of $E_{22}(\underline{q})$ over a discrete set of reciprocal space vectors and an integral of $E_{22}(\underline{q})$ over all values of

$\underline{q}$ below the cut-off in reciprocal space. The above analysis suggests that our formalism is better suited to the determination of the shape of the energy-wavenumber characteristics than the actual magnitudes. Formally, one might expect that the best estimate of the electron contribution to the ordering energy would be the difference between the disordered total energy calculated using the disordered crystalline core energies and the ordered total energy calculated using the ordered crystalline core energies. This would lead to a conduction electron contribution to the ordering energy of 0.098303 rydbergs. However, our previous discussion suggests that the lack of convergence of our perturbation theory expansion would enter strongly into this estimate of the conduction electron contribution, yielding a minimum error of $\pm$ 0.025 rydbergs. Thus we expect that a much better estimate would be obtained by averaging the values for this quantity calculated from the ordered crystalline and disordered crystalline core energies. This leads to an estimate of 0.0743 rydbergs with a minimum error of $\pm$ 0.0005 rydbergs.

Similarly, we may evaluate the effective pairwise interactions between the ions as defined in Equations (2.89), (2.90), and (2.91). We observed large variations in the contributions to the total conduction electron energy which we listed in Table 5.12, depending upon which set of core energies were used in calculating the matrix elements of the pseudopotential. Accordingly, we have selected a particular set of values for use in calculating the effective pairwise

interactions. We have taken the average of the energy-wavenumber characteristics derived from the ordered crystalline and from the disordered crystalline core energies. These averaged energy-wavenumber characteristics yield the effective pairwise interactions which we have displayed in Figure 5.1. These quantities are essentially energies per bond as a function of the length of the bond. Considering nearest neighbors, the alloy which we are considering loses two A-B bonds per ion and gains one A-A bond and one B-B bond when the crystal changes from a completely ordered state to a completely disordered state. For nearest neighbors, V_{Li-Li} = 2.31 millirydbergs (mry.), V_{Li-Mg} = 5.47 mry., and V_{Mg-Mg} = 12.04 mry. Therefore, the nearest neighbors contribute about -3.41 mry. per ion to the ordering energy of the crystal. If we include next nearest neighbors, this alloy gains 3/2 A-B bonds per ion and loses 3/4 A-A bonds and 3/4 B-B bonds during the transition from the ordered to the disordered state. For next nearest neighbors, V_{Li-Li} = 0.86 mry., V_{Li-Mg} = 1.58 mry., and V_{Mg-Mg} = 2.64 mry. Therefore, the next nearest neighbors contribute about +0.34 to the ordering energy. The contributions of these two sets of neighbors to the ordering energy is about -3.07 mry. per ion.

We may now compare the form of our effective pairwise interactions with the form derived by Harrison and Paskin [7]. They suggested that a form of $\cos(2k_F r)/r^3$ was appropriate for even nearest neighbor interactions. We have noted the distances associated with nearest and next nearest neighbors for our alloy on the graph of the effective pairwise interactions. The shape of our expressions for

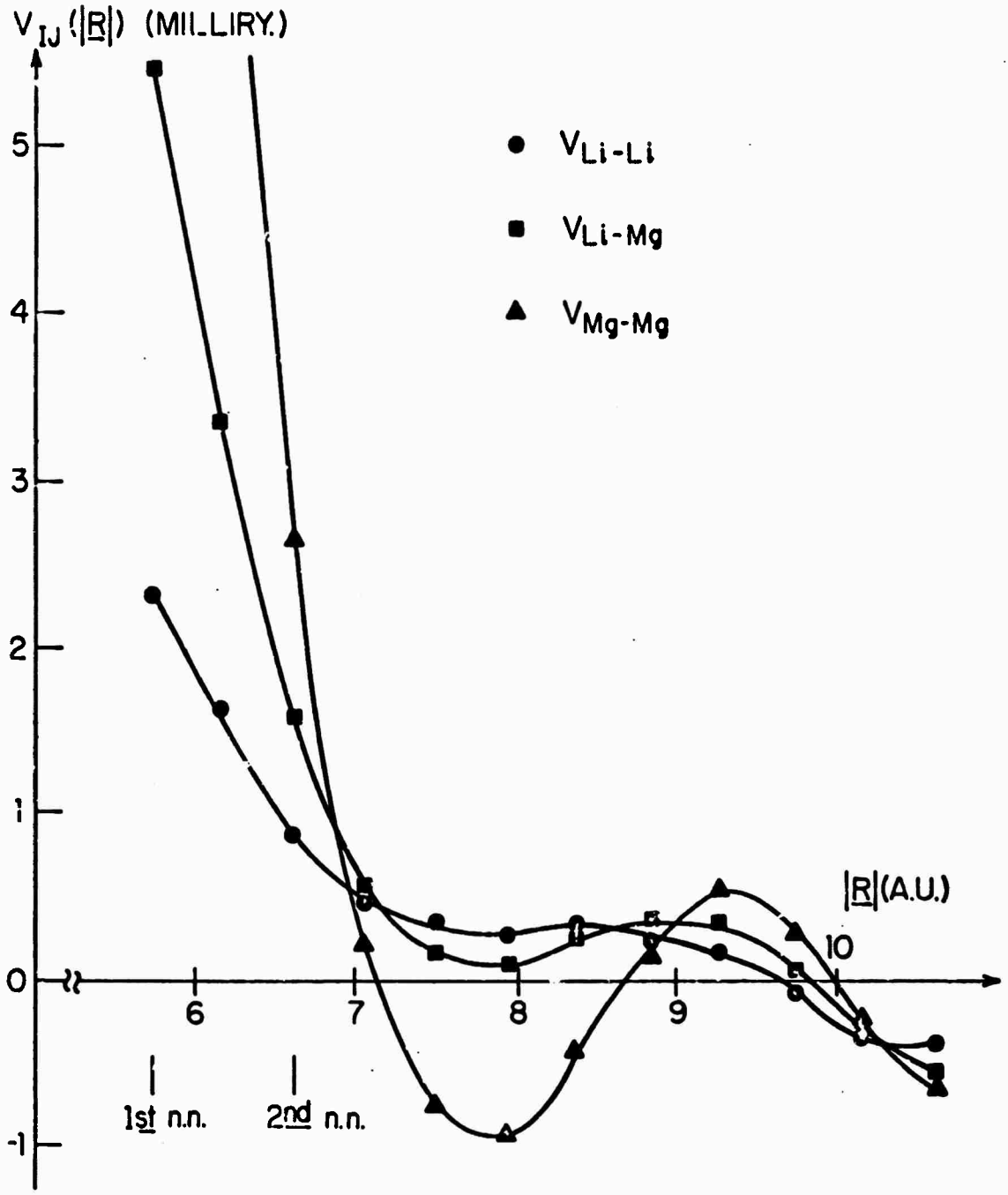

FIG. 5-1 EFFECTIVE PAIRWISE INTERACTIONS BETWEEN THE IONS IN Li-Mg.

these interactions is certainly not $\cos(2k_F R)/R^3$ for values of R including many sets of neighbors. Since the error in our calculation becomes larger with large R, we are unable to predict just when the effective pairwise interactions might attain this asymptotic form.

We may also compare our estimate of the ordering energy using Mott's calculation and experimental observations regarding the behavior of 50-50 lithium-magnesium. For a system with nearest neighbor interactions only, Mott [8] found that the ordering energy should be greater than $-kT_c \ln(2)$, where T_c is the critical temperature. The critical temperature of 50-50 lithium-magnesium could be no higher than about 370°K, or more pronounced short range order would have been observed in the system [9]. This reasoning would indicate that the magnitude of the ordering energy should be less than 0.0017 rydbergs per ion. Our estimate of the ordering energy on the basis of nearest and next nearest neighbors is -0.0031 rydbergs. Part of this discrepancy might be due to the dependence of the ordering in our system upon interactions with many sets of neighbors. The thermodynamic arguments which led to the Mott expression for the upper limit on the ordering energy are not valid for a system in which there are interactions which are other than nearest neighbor. In addition, we have not considered the effect of the change in ionic volume when the system orders. This effect might be expected to lessen the difference in energy between the ordered and disordered states, and would therefore be a correction in the right direction.

We may obtain an expression for the ordering energy which takes into account the interactions between all sets of neighbors by adding the total conduction electron contribution and the ionic contribution to the ordering energy. Our expression for the conduction electron contribution includes the effect of the full conduction electron charge distribution, and therefore includes the effect of the charge orthogonalized to the ions. Thus the ionic contribution to the ordering energy consists of a Madelung interaction of actual ionic charges, not effective charges. The Madelung energy is roughly -0.0769 rydbergs for an array of charges of magnitude $\pm 1/2$ in the cesium chloride structure with a lattice constant of 3.5 Å. When the lattice disorders, the Madelung energy of this array vanishes. Accordingly, we may combine the above energy with the more accurate estimate of the conduction electron contribution which we discussed previously to obtain an ordering energy of -0.0026 rydbergs. We may note that the larger estimate of the conduction electron contribution to the ordering energy, which we found by taking the difference between the energies in two separate columns in Table 5.12, leads to our expecting the disordered state to be the ground state. This underscores our discussion regarding the unreliability of this procedure for estimating the conduction electron contribution to the ordering energy. In conclusion, a reasonable interpretation of our results has led to an estimate of the ordering energy which is consistent with experimental observations on the system if one allows for the neglect of volume changes and the inapplicability of the thermodynamic relation between T_c and the ordering energy.

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Chapter Six

CONCLUSIONS

The results of the calculations which we described in Chapter Five demonstrate that our expression for the structure-dependent part of the total conduction electron energy is quite sensitive to the choice of core eigenvalues in the alloy. This behavior is attributed to the inaccuracy of our perturbation expansion of the total conduction electron energy to second order in the pseudopotential. We might expect that this expression for the energy will be sensitive in a similar manner to the particular choice of a form for the pseudopotential, as discussed in Chapter Four. Accordingly, we must stress the importance of choosing the optimal form for the pseudopotential with care.

The estimate of the total conduction electron energy is so sensitive to the choice of pseudopotential that we must expect an error of at least $\pm$ 0.013 rydbergs for a given set of core energies. This minimum error is somewhat too large for an accurate determination of the cohesive energy. However, our estimate of the conduction electron contribution to the ordering energy is much less sensitive to the choice of pseudopotential. The minimum error in this quantity is only $\pm$ 0.0005 rydbergs, which is small enough to allow a reasonable estimate of the ordering energy. Therefore, our formalism appears to yield reasonably accurate values for those quantities which depend upon the difference between two evaluations at the same ionic volume

of a given conduction electron property, such as the ordering energy. We might also expect that our formalism would be suitable for a calculation of the difference in cohesive energy between two crystalline structures with the same ionic volume, or for a calculation of the increase in alloy resistivity upon disordering.

Our estimate of the ordering energy may be considered as a sum over the effective pairwise interactions between all the ions. Therefore, we must conclude that these central force interactions represent quite well those interactions which lead to the formation of the superlattice in a 50-50 alloy of lithium and magnesium. However, the effective pairwise interactions which we have calculated do not attain the simple form suggested by Harrison and Paskin until well beyond first and second nearest neighbor distances.

We might note that our evaluation of the results of this formalism is based on the reasonable assumption that this alloy of lithium and magnesium would actually attain an ordered state if its critical temperature were not so low that the disordered state is "frozen" in the crystal as the temperature is lowered. Our theoretical results have definitely indicated that the ordered state is the ground state at the absolute zero of temperature. Accordingly it would be instructive to artificially increase the movement of the ions in the alloy by subjecting it to appropriate radiation while at temperatures below its expected critical temperature. The ions may then reach equilibrium distributions at these low temperatures. This experiment should allow a determination of the

critical temperature and thereby provide a comparison with our theoretical results.

The essential limitation of our formalism appears to be associated with the use of perturbation theory. It does not appear that any other approximation which we have made affects our results as strongly as our use of perturbation theory. While the approximation of the screening potential in terms of a first order expression is central to most of the pseudopotential formalism, we might improve our results by using the hybrid mixture of perturbation theory and matrix diagonalization which we discussed in Chapter Three. This procedure would yield accurate energies for the individual electrons in the region of the lowest energy band gap which appears as the system orders. These energies might then be used to obtain a more accurate estimate of the total conduction electron energy. This use of first order perturbation theory to find the screening potential followed by a limited matrix diagonalizati[illegible]e similar to a limited self-consistent procedure. In any case, any significant improvement in the results of this formalism will most likely be brought about through an improvement in the accuracy of our perturbation expansions.

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13. ABSTRACT

The pseudopotential formalism which has been developed to calculate the properties of periodic crystals is extended to treat the case of a binary alloy with an arbitrary degree of order. A self-consistent screening potential which includes the effect of the total conduction electron charge is derived to first order in a perturbation theory expansion in the pseudopotential. The conduction electron contribution to the total energy of the crystal is expressed to second order in the pseudopotential. The applicability of these perturbation theory expansions is discussed extensively. Expressions for that part of the conduction electron energy which contributes to the ordering energy and for the effective pairwise interactions between the ions in the alloy are derived from the expression for the total energy.

If the conduction electron energy may be expressed accurately to second order in the pseudopotential, we demonstrate that this energy depends only upon correlations between pairs of ions. Otherwise, accurate individual electron energies near band gaps are shown to depend upon correlations between three or more ions for an alloy below its critical temperature.

The procedure for selecting an optimal form for the pseudopotential is examined in detail. A Hermitian pseudopotential is chosen and its advantages are discussed. Our calculations on a 50-50 alloy of lithium and magnesium indicate that the selection of an appropriate pseudopotential is quite important.

Further, the calculations reveal that this formalism may be expected to yield accurate estimates only for those quantities which depend upon the difference between two evaluations at the same ionic volume of a given conduction electron property in the alloy, such as the ordering energy. Therefore, we might calculate with accuracy the differences in cohesive energy between two structures with the same volume per ion, or the alloy resistivity, but not the cohesive energy itself. In addition, the effective pairwise interactions are shown to represent well those interactions in the alloy which contribute significantly to the formation of the superlattice.

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